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Fig. 1.
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Curve 1

Curve 2
Curve 3
Curve 4
Curve 5

PHOTOGRAPHIC SCIENCE AND ENGINEERING
Volume 2, Number 3, October 1958

Sensitization of Mercurous Oxalate by Dyes

P. A. VAN DER MEULEN AND ROBERT H. BRILL, *Ralph G. Wright Laboratory, School of Chemistry, Rutgers, The State University, New Brunswick, N.J.*

The adsorption of several sensitizing dyes by mercurous oxalate has been determined. The reflectance spectra of mercurous oxalate with adsorbed dye have been measured. Adsorption is often accompanied by a bathochromic shift of the absorption maxima. The best sensitizers found are Acriflavine, Acridine Orange, Acridine Yellow, and Proflavine, and all are strongly adsorbed. Pyronin B and Acridine Red are weakly adsorbed and are feeble sensitizers. In the case of the phthalein dyes the order of sensitization is Erythrosin B > Eosin Y > Rose Bengal > Phloxin B. Erythrosin B, a better sensitizer than Eosin Y, is more strongly adsorbed, but Rose Bengal does not sensitize as well as Eosin Y even though it is more strongly adsorbed. The cyanine dyes are not notably better sensitizers for mercurous oxalate than the other classes of dyes studied. In general, the spectral range of sensitization for mercurous oxalate by a given dye is virtually the same as the range for silver halide emulsions.

PART I — Adsorption of Certain Dyes by Mercurous Oxalate

The sensitivity of a photothermographic emulsion consisting of mercurous oxalate suspended in gelatin lies in the near-ultraviolet region of the spectrum. Preliminary results obtained in an effort to increase the inherent spectral sensitivity of mercurous oxalate were reported by van der Meulen and Countryman.[1] It was shown that certain dyes produce sensitization in the visible region of the spectrum. Since adsorption is known to be an important factor in the optical sensitization of silver-halide emulsions,[2] a systematic study was made of the adsorption of a number of sensitizing dyes by mercurous oxalate. The results of this study are reported in this paper.

Received 7 March 1958.
The work described is based on a thesis submitted to the Graduate Faculty of Rutgers, The State University, by Robert H. Brill in partial fulfillment of the requirements for the degree of Doctor of Philosophy. The work was carried out in part under contract DA36-039-SC15560 with the Squier Signal Laboratory, Photographic Branch, Fort Monmouth, N.J., and in part under contract AF18-(600)1150, Air Force Office of Scientific Research, Washington 25, D.C.

Experimental Procedure

A stock solution of mercurous nitrate was prepared by dissolving 21 grams of the freshly-recrystallized salt in 120 ml of 0.3–N HNO_3; 51.6 grams of reagent-grade $K_2C_2O_4 \cdot 2H_2O$ were dissolved in 160 ml of water. One-half gram of mercurous oxalate was precipitated

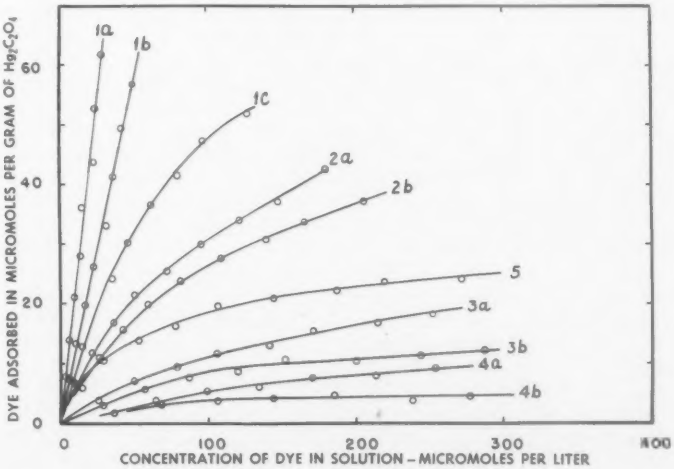


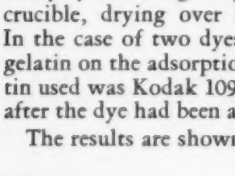
Fig. 1. Adsorption isotherms of dyes on mercurous oxalate, from solution in water.
Curve 1 — Erythrosin B: a at 7 C; b at 27 C; c at 27 C in presence of 0.46% gelatin.
Curve 2 — Rose Bengal: a at 7 C; b at 27 C.
Curve 3 — Eosin Y: a at 7 C; b at 27 C.
Curve 4 — Phloxin B: a at 7 C; b at 27 C.
Curve 5 — Acridine Orange: at 22.5 C.

in each of several 100-ml volumetric flasks by placing in each flask sufficient potassium oxalate solution to provide a 600% excess, and adding the required quantity of mercurous nitrate solution. The precipitates were washed by decantation with two 100-ml portions of distilled water, and then 50 ml of distilled water were added. (This procedure leaves a small excess of oxalate ion in the solution required to produce a sensitive product.) To these suspensions were added the required quantities of dye.* In all except two cases the dyes were sufficiently soluble in water, and this was the solvent used. Two dyes required 15 weight per cent of ethanol, and in these cases this ethanol concentration in water was used throughout the procedures. The flasks were placed in a thermostat for a few hours until equilibrium had been attained. The final dye concentrations were determined by the use of a Beckman D.U. spectrophotometer and the quantity of dye adsorbed was calculated from the change in dye concentration. Finally, the weight of mercurous oxalate was determined accurately by collecting the precipitates on a sintered glass crucible, drying over sulfuric acid, and weighing. In the case of two dyes the effect of the addition of gelatin on the adsorption was determined. The gelatin used was Kodak 1099, and was added to the flasks after the dye had been added.

The results are shown graphically in Figs. 1 and 2.

Discussion

The adsorption of the phthalein dyes reveals an orderly sequence.



The substituents in the four dyes are as follows:

	Substituent and Position	
Erythrosin B	A = H	B = I
Rose Bengal	A = Cl	B = I
Eosin Y	A = H	B = Br
Phloxin B	A = Cl	B = Br

The order of adsorption is Erythrosin B > Rose Bengal > Eosin Y > Phloxin B. This suggests that the iodine atoms in the first two dyes lead to greater adsorption than the bromine atoms in the last two. The data also indicate that the substitution of chlorine atoms in the phthalic anhydride part of the compound reduces the tendency to be adsorbed. Curves 1*b* and 1*c* (Fig. 1) indicate that gelatin reduces the adsorption of Erythrosin B.

The cyanine dyes which contain selenium are more strongly adsorbed than those containing sulfur. A comparison of Curves 2*b* and 2*c* (Fig. 2) shows that in this case, also, gelatin reduces the adsorption of the dye.

* The cyanine dyes were supplied by E. I. du Pont de Nemours & Company, Inc., Parlin, N.J., and the fluorescein and acridine dyes by the National Aniline Division of Allied Chemical and Dye Corp.

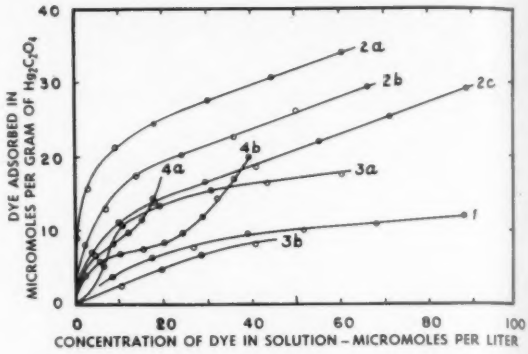


Fig. 2. Adsorption isotherms of dyes on mercurous oxalate.
Curve 1 — 3,3′,9-Triethylthiacarbocyanine at 9.5 C (from water solution).
Curve 2 — 3,3′,9-Triethylselenacarbocyanine: *a* at 7.5 C; *b* at 26.5 C; *c* at 26.5 C in presence of 0.46% gelatin (from water solution).
Curve 3 — 3,3′-Diethylthiacarbocyanine (from 15% ethanol solution): *a* at 20.4 C; *b* at 41.8 C.
Curve 4 — 3,3′-Diethylselenacarbocyanine (from 15% ethanol solution): *a* at 28.5 C; *b* at 42.5 C.

Absorption of Light by Dyed Mercurous Oxalate

The reflectance spectra of several of the dyed precipitates of mercurous oxalate recovered from the adsorption experiments were measured with the reflectance attachment of a Beckman Spectrophotometer. The reflectance of an undyed sample was also measured. The values of the absolute reflectances were subtracted from 100% to arrive at an estimate of the per cent of total incident energy absorbed. In order to observe the change in spectrum caused by dye adsorption, the energy-absorption curve for an undyed sample of mercurous oxalate was substracted from that of the dyed samples, yielding a quantity which has been designated as ΔE_a. This quantity is a measure of the additional per cent of incident energy of any wavelength absorbed due to the presence of dye adsorbed to the mercurous oxalate surface. Plots of ΔE_a vs. wavelength are shown in Fig. 3. For samples with low dye coverage it is possible to estimate absorption peaks even though the peaks are not sharply defined as compared to the spectra of the dyes in solution. It will be noted that the curves for the two cyanine dyes exhibit two peaks. The curve shown for Erythrosin B is typical of the results obtained with the phthalein dyes.

Table I summarizes the results of these experiments. It can be seen that a bathochromic shift of λ_{max} accompanies the adsorption of these dyes from aqueous solution. The average for the four phthaleins is a shift of +18 mμ. Natanson[3] has reported that the shift in λ_{max} for Erythrosin B is +25 mμ when that dye is adsorbed on silver bromide and +21 mμ in the case of Phloxin. 3,3′,9-Triethylthiacarbocyanine shows a shift of +8 mμ and 3,3′,9-triethylselenacarbocyanine a shift of +29 mμ if comparisons are made between the monomeric peaks in dilute solution and

the longer-wavelength peaks in the adsorbed state. These shifts become +60 mμ and +70 mμ if the comparisons are made between the H-bands in more concentrated solutions and the longer-wavelength peaks in the adsorbed state. The shorter-wavelength peaks in the adsorbed state could possibly represent a bathochromic shift from solution peaks in the ultraviolet or possibly hypsochromic shifts of the H-bands in solution corresponding respectively to changes of −90 mμ and −65 mμ.

PART II — Sensitization by Dyes

In Part I above, the adsorption of a number of dyes by mercurous oxalate was described. The sensitization produced by these and a few additional dyes in emulsions has been investigated and the results are described below.

Experimental Procedure

Three stock solutions were prepared. The first contained 126 grams of freshly recrystallized $Hg_2(NO_3)_2$ dissolved in 720 ml of 0.3-N HNO_3. The second contained 309.6 grams of reagent-grade $K_2C_2O_4 \cdot H_2O$ dissolved in 960 ml H_2O. The third contained 113 grams of gelatin (Kodak 1099) dissolved in water and made up to a total volume of 1 liter.

Working entirely under darkroom conditions, the first solution was added slowly, with vigorous stirring, to the second solution. The suspension of mercurous oxalate was stirred for 10 min, and was then passed three times through a homogenizer. The suspension was washed by decantation with five 2-liter portions of distilled water and made up to 1360 ml. While the suspension was being agitated vigorously, 25-ml portions were removed with a pipette and transferred to small sample jars. An equal volume of water (25 ml) containing the dye under investigation was added to the suspension and the samples were allowed to stand overnight. Forty milliliters of the supernatant liquid were removed, the dye concentration determined spectrophotometrically, and the quantity of dye adsorbed by the mercurous oxalate calculated. To the remaining suspension, 35 ml of gelatin solution was added with stirring, and then 5 ml of water, producing a final suspension with a volume of 50 ml. This was passed through a homogenizer and stored in a refrigerator.

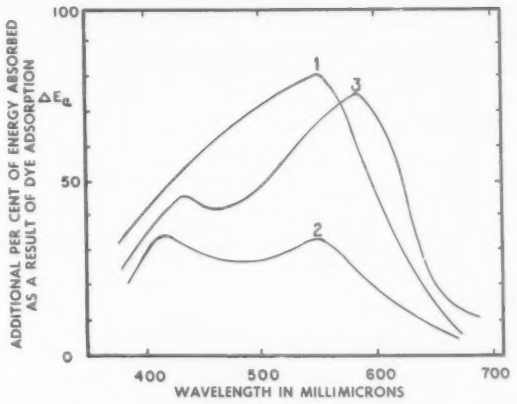


Fig. 3. Plot of ΔE_a vs. wavelength for dyed $Hg_2C_2O_4$. Additional per cent of incident energy absorbed as a result of adsorption of dye to $Hg_2C_2O_4$.
Curve 1 — Erythrosin B; 6.4 micromoles dye/gram $Hg_2C_2O_4$.
Curve 2 — 3,3′,9-Triethylthiacarbocyanine; 1.8 micromoles dye/gram $Hg_2C_2O_4$.
Curve 3 — 3,3′,9-Triethylselenacarbocyanine; 7.2 micromoles dye/gram $Hg_2C_2O_4$.

A separate determination of the content of mercurous oxalate in 25 ml of this original suspension showed that this was 2.02 grams.

The stock emulsions were liquefied by warming at 40–50 C, and strained through cheese cloth. One-milliliter portions were transferred to 7.5 × 2.8-cm glass slides, distributed uniformly, and chilled on a leveled metal plate. As soon as the emulsion had set, the slides were placed in a refrigerator to dry.

Light Sources, Exposure, and Development

The tungsten lamp supplied with the Beckman D.U. Spectrophotometer is a convenient light source

TABLE I

Dye	Spectrum in Solution: Concn. in μmoles/liter	Spectrum in Solution: λ_{max}	Spectrum in Adsorbed State: λ_{max} in ΔE_a curve	Spectrum in Adsorbed State: m μmoles Dye/gram $Hg_2C_2O_4$	C μmole/liter	Shift Due to Adsorption
Triethylthia-carbocyanine	4.0	542	550, 415	1.8	2.5	+ 8 (dil.)
	200.0	505	565, 430	10.7	100.0	+60 (concn.)
Triethylselena-carbocyanine	2.0	556	585, 430	7.2	1.0	+29 (dil.)
	100.0	495	565	26.2	56.0	+70 (concn.)
Eosin Y	6.36	521	540	2.6	17.0	+19
Phloxin B	5.00	542	555	2.3	22.0	+13
Erythrosin B	4.94	531	554	6.4	4.0	+23
Rose Bengal	4.24	552	570	5.2	10.0	+18

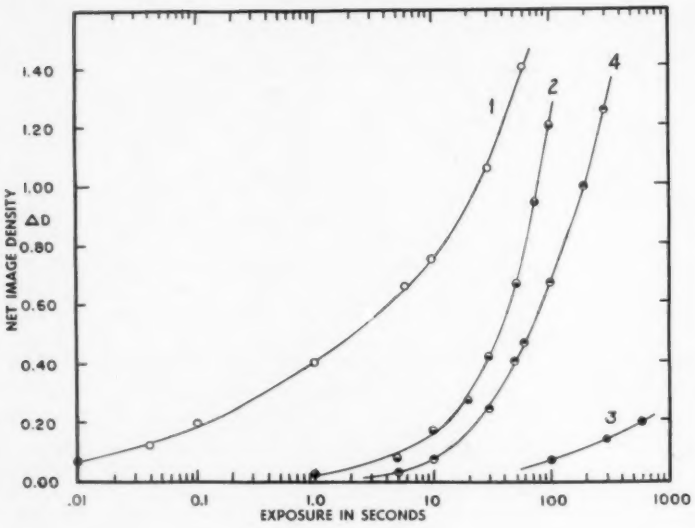


Fig. 4. ΔD versus log exposure for $Hg_2C_2O_4$ emulsions. Intensity = 131 μw/sq cm.
Curve 1 — 254 mμ, undyed.
Curve 2 — 366 mμ, undyed.
Curve 3 — 460 mμ, undyed.
Curve 4 — 460 mμ, dyed with Acridine Orange.

for sensitization studies. The monochromator of the instrument provides a reasonably intense and homogeneous beam of light of any desired wavelength from 360 mμ through the visible region. The intensity of the beam is easily adjusted by changing the slit width. For our purpose the slit-width required to produce an arbitrary intensity of 131 μw/sq cm was determined, for various wavelengths, by means of a bismuth-silver thermopile, and this intensity was used for all exposures.

The coated slides were mounted in a small brass jig which fitted snugly in the cell carrier of the spectrophotometer, and, by using the filter slide of the instrument as a shutter, five or six exposures were made, on the same slide, to different wavelengths of radiation. Each exposure was made for 300 sec. To measure the inherent sensitivity in the ultraviolet region of mercurous oxalate without sensitizing dye, two lamps were used.[4] One of these emits principally the 2537Å mercury line, and the other the 3660Å line. Exposures were made at distances at which the intensity was 131 μw/sq cm, as indicated by the thermopile.

After exposure the slides were developed by heating for 30 sec at 120 C in an oven described by van der Meulen and Countryman.[1] The optical density of adjacent exposed and unexposed portions of the slides was read visually by means of a Kodak Color Densitometer, using the green filter of the instrument. The difference in density, ΔD, of the exposed and unexposed portions constitutes a direct measure of the photothermographic action.

Spectral Sensitivity of Undyed Mercurous Oxalate Emulsions

In order to locate the inherent spectral sensitivity of mercurous oxalate, the response of an undyed emulsion to ultraviolet radiation was determined. The results for wavelengths of 254 mμ, 366 mμ, and 460 mμ are given in Fig. 4. A 300-sec exposure to 500 mμ radiation yields no observable image after development. Curve 4 shows the typical response of a dyed emulsion to radiation corresponding to its sensitivity peak in the visible region. The transmission spectrum of mercurous oxalate suspended in gelatin or collodion and the reflectance spectrum of undyed solid mercurous oxalate show a trend towards much stronger absorption in the middle ultraviolet than in the near ultraviolet and visible, particularly below 250 mμ. It is therefore reasonable to expect the photothermal sensitivity to be centered there.

Evaluation of the Sensitizing Power of Dyes

The photothermal images produced in the emulsions under study consist of mercury trapped in gelatin, along with some undecomposed mercurous oxalate. To express the extent of photothermographic action, it is necessary to select some scheme which indicates the quantity of mercury produced, and to relate this to the exposure and development conditions utilized to produce that mercury. One such scheme is to plot the net image density, ΔD, vs. exposure. For a constant intensity and development procedure, mercurous oxalate emulsions yield curves which resemble the characteristic curves of silver-halide emulsions, except that the sensitivities are much lower. In order to describe the spectral response of a dye-sensitized emulsion it is convenient to plot the ΔD attained for some standard exposure and development as a function of the wavelength of the exciting radiation.

The sensitizing powers of several classes of dyes were compared by preparing and testing thirty-five emulsions containing twenty-four different dyes. Each dye was studied by adding an initial 100 μmoles of

TABLE II

Dye	μmoles Dye/gram $Hg_2C_2O_4$ in the Emulsion	Range Sensitized (mμ)	Silver-Halide Sensitization*
Acridine Orange	2.45	420-460-580	470-510-550
Acridine Orange	1.20	460-500-580	———
Proflavine	2.50	420-450-550	———
Acridine Yellow	2.50	420-460-580	———
Acriflavine	2.50	420-480-580	———
Pyronin B	1.82	530-560-590	———
Acridine Red	1.36	480-550-580	———
Thionin	2.10	540-630-680	———
Fluorescein	2.50	460-490-560	———
Erythrosin B	2.46	480-560-610	480-560-590
Erythrosin B	0.64	480-560-610	———
Rose Bengal	2.27	500-570-610	———
Eosin Y	1.62	470-540-580	———
Phloxin B	1.52	480-550-590	———
Gallein	2.50	No sensitization	———
3,3′-Diethylthiacarbocyanine	2.50	470-550-630	480-580-630
3,3′-Diethylselenacarbocyanine	2.50	460-590-640	490-600-650
3,3′,9-Triethylthiacarbocyanine	2.50	530-570-600	———
3,3′,9-Triethylselenacarbocyanine	2.50	480-580-640	585
3,3′-Diethyloxacarbocyanine	2.44	very slight at 500	450-520-550
1,3-Diethylthia-2′-cyanine	2.30	440-480-570	———
Astraphloxine	1.17	460-550-620	———
Pinacyanol	2.50	480-520-650	510-630-670
Pinaflavol	1.07	490-530-580	470-520-570
Diethylaminostyryl-2(3-ethyl-5-chlorobenzothiazole)	>2.40 >2.50	480-550-610	490
Diethylaminostyryl-2(3-ethyl-5-chlorobenzoselenazole)	2.50	480-540-610	———

*C. E. K. Mees, *The Theory of the Photographic Process*, Macmillan Company, New York, 1954, Chap. X.

dye per liter of final emulsion, and a few dyes were studied at other concentrations as well. The greater portion of the unadsorbed dye (80%) was removed before the addition of gelatin so that it would not act as a light filter in the final emulsion and prevent light from reaching the dyed grains. Two undyed emulsions served as controls.

Plots of ΔD vs. wavelength are shown in Fig. 5–8, and the data are summarized in Table II.

It appears that the group of dyes Acriflavine, Acridine Orange, Acridine Yellow, and Proflavine are the best sensitizers. All four of these dyes were completely adsorbed under the experimental conditions. Pyronin B and Acridine Red, which are only weakly adsorbed, are poor sensitizers. Thionin, which is rather strongly adsorbed, confers only slight sensitization which is centered in the red region. As a general rule, those dyes which sensitize towards the red are less effective than those which sensitize in the blue region. The sensitizing mechanism appears to be less efficient for less energetic radiation.

The phthalein dyes show a trend in sensitizing power related to their structures. The order is Erythrosin B > Eosin Y > Rose Bengal > Phloxin B. The two dyes with chlorine atoms substituted in the phthalic anhydride part of the molecule (RB and PB) are not as effective as the unsubstituted dyes (EB and EY). In addition Erythrosin B is a better sensitizer than Eosin Y, which is not as strongly adsorbed. Rose Bengal, however, is more strongly adsorbed than Eosin Y but does not sensitize as well. This suggests that the desensitizing effect of the chlorine atoms outweighs the beneficial effect of increased adsorption. Similar behavior has been noted in the silver-halide systems. Schwarz[5] has reported that sensitizing increases as the xanthene structure is substituted, and decreases as the phthalein ring is halogenated.

It was found that fluorescein itself sensitizes to an extent which compares favorably with its derivatives. The ability of fluorescein to sensitize is somewhat unexpected in view of the fact that dyes which fluoresce strongly are generally regarded as poor sensitizers. It has been observed, however, that the fluorescence of fluorescein is completely quenched when it is adsorbed to mercurous oxalate. This is true of all the dyes used in this study.

The cyanine dyes, in general, are not notably better sensitizers for mercurous oxalate than the other classes of dyes studied. The selenacarbocyanines are somewhat superior to the thiacarbocyanines, and they are also more strongly adsorbed. The styryl dyes, along with pinaflavol and pinacyanol, are only weak sensitizers. Although 3,3′-diethyloxacarbocyanine was strongly adsorbed, it showed very little sensitizing activity.

The peaks in the sensitization curves coincide (within 5 mμ) with the maxima in the energy-absorption spectra discussed in Part I of this paper. Table

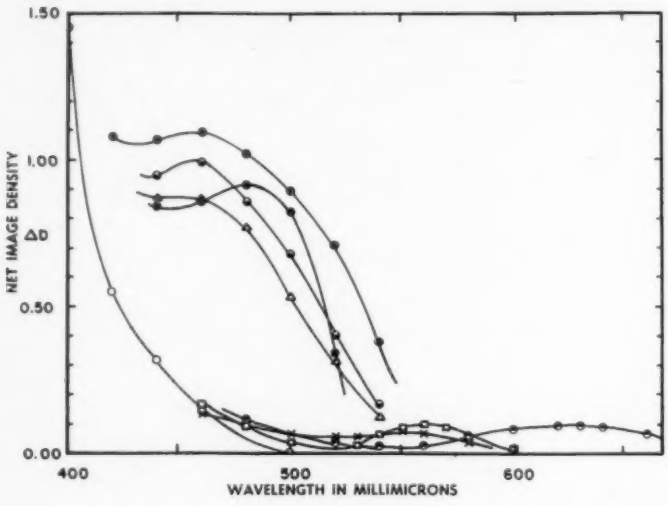


Fig. 5. Spectral response of dyed emulsions.
O — Undyed
⊕ — Acridine Orange
◒ — Acridine Yellow
● — Acriflavine
△ — Proflavine
◓ — Thionin
□ — Pyronin B
× — Acridine Red

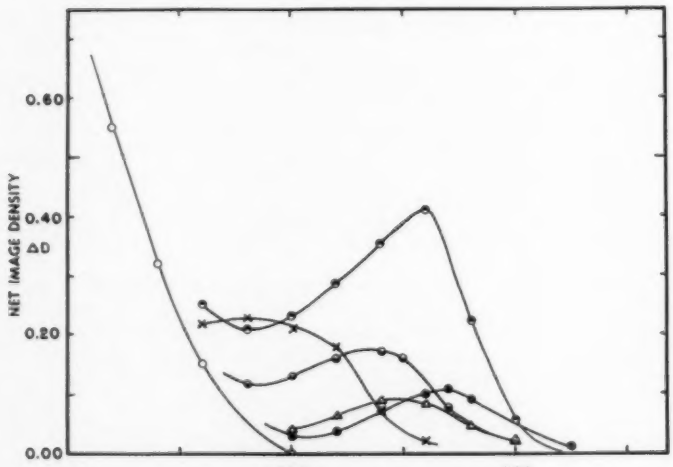


Fig. 6. Spectral response of dyed emulsions.
O — Undyed
◓ — Erythrosin B
● — Rose Bengal
◒ — Eosin Y
△ — Phloxin B
× — Fluorescein

II shows that for mercurous oxalate the range sensitized by a given dye is virtually the same as the range to which the dye sensitizes silver-halide emulsions.

Sensitization by Dye Mixtures

The influence of adsorption on sensitization was further demonstrated by using mixtures of two dyes and comparing their combined effectiveness with that of the single dyes. It was found that the addition of Erythrosin B, a dye which is very strongly adsorbed, to an emulsion dyed with Acridine Orange, caused a pronounced shift in the resulting sensitivity from the region sensitized by Acridine Orange to that sensitized by Erythrosin B. The addition of Phloxin B, which is not as strongly adsorbed as Erythrosin B or Acridine Orange, does not similarly reduce the sensitization by Acridine Orange, nor does it sensitize the resulting emulsion to its own normal sensitizing range.

Estimation of Quantum Yields

In order to calculate quantum yields for the photothermographic processes described it is necessary to determine the photometric equivalent of the mercury produced, that is, to establish the dependence of the optical density of an image on the concentration of mercury in that image. Because of the very minute quantities of mercury involved, and the uncertainty in the nature of light absorption by mixtures of mercury and the undecomposed mercurous oxalate crystals, many complications arise in the determinations of the photometric equivalent of the mercury. A further complication arises from the volatilization, even

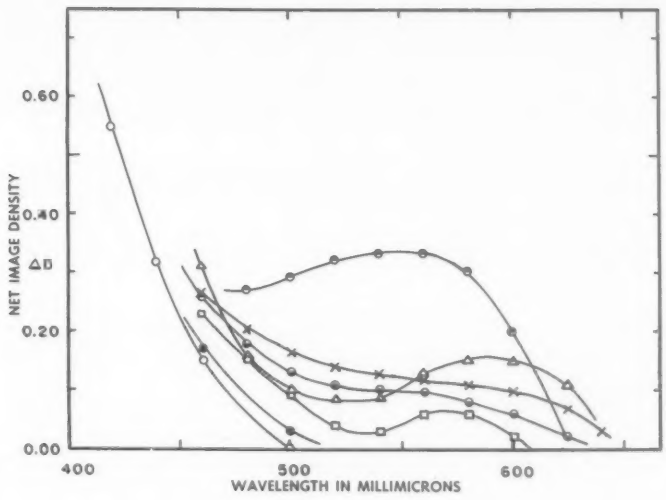


Fig. 7. Spectral response of dyed emulsions.
O — Undyed
◒ — 3,3′-Diethylthiacarbocyanine
△ — 3,3′-Diethylselenacarbocyanine
□ — 3,3′,9-Triethylthiacarbocyanine
X — 3,3′,9-Triethylselenacarbocyanine
● — 3,3′-Diethyloxacarbocyanine
◓ — Astraphloxine

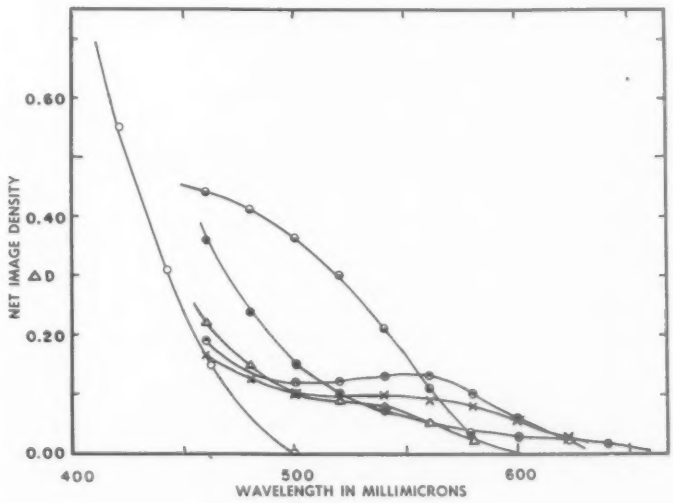


Fig. 8. Spectral response of dyed emulsions.
O — Undyed
◒ — 1,3-Diethylthia-2′-cyanine
● — Pinacyanol
◓ — Diethylaminostyryl-2(3-ethyl-5-chlorobenzothiazole)
X — Diethylaminostyryl-2(3-ethyl-5-chlorobenzoselenazole)
△ — Pinaflavol

though slight, of the mercury during development. Nevertheless, estimates have been made which indicate that the quantum yields for the over-all photothermographic process, including standard development, probably range from about 0.5 to 5.0 atoms of mercury per quantum absorbed. These values correspond to the data presented in Figs. 5–8 for the standard testing treatment applied to the dyed emulsions.

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Relation Between Accelerating and Retarding Tendencies of Some Active Substances in Physical Ripening of Silver Chloride Suspensions

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The effects of N-alkyl derivatives of benzothiazoline-2-thione, quinoline-2-thione, and benzimidazoline-2-thione on the physical ripening of silver chloride emulsions were tested. The retarding activities of the compounds were determined on emulsions which were prepared with a mixture of polyvinyl alcohol and polyvinyl pyrrolidone as a substitute for gelatin. All the methyl derivatives are very active retarders, whereas the ethyl derivatives are very active accelerators of physical ripening.

It is well known that many compounds which contain the –SH group, such as l-cysteine, 2-mercaptobenzothiazole, 2-mercaptobenzimidazole, and thiouracil, usually retard the physical ripening of silver halide–gelatin emulsions. As the authors pointed out earlier,[1] however, if the compounds are added to an emulsion prepared with polyvinyl alcohol instead of gelatin, their retarding action is not appreciable at the usual concentrations because of the extraordinarily powerful retarding action of polyvinyl alcohol itself, and an acceleration appears at somewhat higher concentrations.

The influences of S-alkylation or N-alkylation upon the activity of benzothiazoline-2-thione when added to a developer were reported before by Oh-Yama.[2] The dual property of the parent substance as an emulsion addition (retardation and acceleration of physical ripening) is also affected by these substitutions, but there is much difference between the behavior of the N-methyl derivative and that of the N-ethyl derivative.

In the present paper, it is shown that the differences between N-methylation and N-ethylation are quite general among some of the related compounds.

Experimental Procedure

The method used to determine the ripening accelerating activity of these substances was described in previous reports.[1,3–6] The retarding properties are determined in almost the same way; the only difference is that polyvinyl pyrrolidone is used together with polyvinyl alcohol (1% of each) as protective colloid instead of polyvinyl alcohol alone. To 37 ml of an aqueous solution of active substance at various concentrations (10 ml of this solution was replaced by alcohol when necessary for slightly soluble substances), 10 ml of 6% solution of polyvinyl alcohol, 5 ml of 12% solution of polyvinyl pyrrolidone and 4 ml of 0.6 molar sodium chloride solution are added. The mixture is heated to 70 C, and 4 ml of 0.2 molar silver nitrate solution (70 C) is added in about 15 sec.

Two-milliliter samples of this suspension of silver chloride are drawn out 2, 4, 8, and 16 min after the addition of silver ions. The samples are diluted with 20 ml of cold water and the turbidity measured. The turbidity measurement adopted in this experiment is the same as that described in the previous reports[1,3,4] and later designated as the K-method.[5] The intensity of a parallel light beam which passes through a glass cuvette (1-cm depth) containing the diluted emulsion is measured with the aid of a photocell at two points (just behind the cuvette and 20 cm away from it), and the turbidity is defined as the relative decrease (%) of deflection of the microammeter in the latter case. The ripening characteristics are represented for both acceleration and retardation by drawing the curves of the turbidities vs. the logarithms of the concentrations of added active substances at appropriate times of ripening.

Results and Discussion

2-Mercaptobenzothiazole

This is a well known fog-inhibitor and physical ripening retarder.[2] The authors found, however, with the usual polyvinyl alcohol–silver chloride emulsion test that 2-mercaptobenzothiazole also has an accelerating action on physical ripening when it is used at somewhat higher concentration (over 0.5–1 millimolar). In this test, however, the retarding prop-

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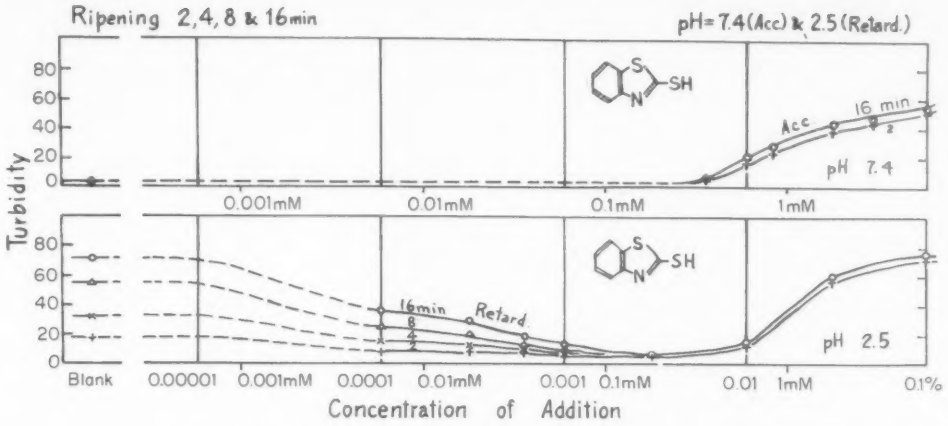

Fig. 1. Accelerating and retarding characteristics of 2-mercaptobenzothiazole.

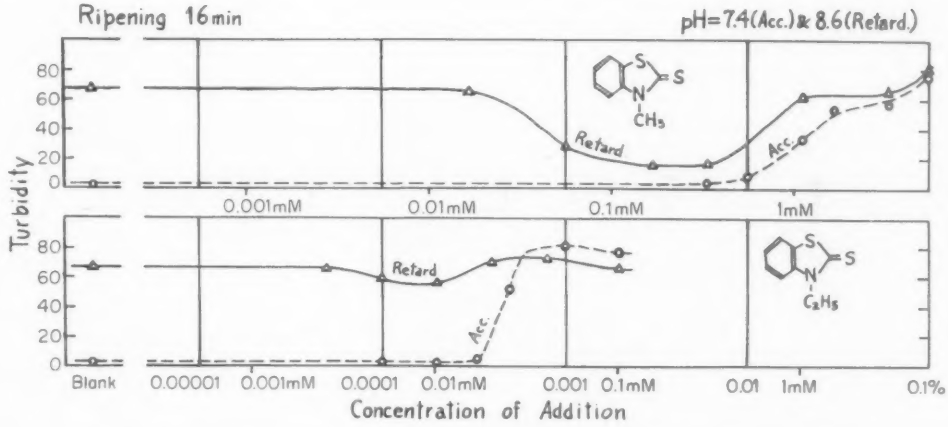

Fig. 2. Accelerating and retarding characteristics of N-methyl- and N-ethyl-benzothiazoline-2-thione.

erty of the compound is hidden by the extraordinarily powerful retarding action of polyvinyl alcohol, but can be revealed by the above mentioned polyvinyl pyrrolidone addition test. The upper part of Fig. 1 illustrates the usual acceleration characteristics shown by the polyvinyl alcohol emulsion test, and the lower part illustrates the retarding characteristics shown by the polyvinyl pyrrolidone addition test. The retarding activity is already appreciable at a very low concentration, as low as 0.001 millimolar (nearly 0.00001%), and this is in accord with its strong adsorption to the surface of the silver halide grains.

N-Methyl and N-Ethyl Derivatives of Benzothiazoline-2-thione, Quinoline-2-thione, and Benzimidazoline-2-thione

The accelerating and retarding dual property of 2-mercaptobenzothiazole is also appreciable in its N-alkyl derivatives, but the effects of the methyl and ethyl derivatives are quite different. Both accelerating and retarding characteristics of the N-methyl and N-ethyl derivatives are shown in Fig. 2. The two characteristic curves obtained after 16 minutes' ripening are illustrated in one figure for each derivative. Only a slight difference, if any, was found between the methyl derivative and the parent compound when compared at the same pH (the curve for the parent compound is not shown for pH 8.6), whereas the influence of the N-ethyl substitution is very apparent, i.e. the accelerating activity is greatly enhanced and the retarding property is scarcely noticeable.

These peculiar influences of N-methyl and N-ethyl substitution are also seen in other substances such as N-alkylquinoline-2-thione and N,N′-dialkylbenzimidazoline-2-thione. Results are shown in Fig. 3 and Fig. 4, respectively.

Possibly these results can be explained by the fact

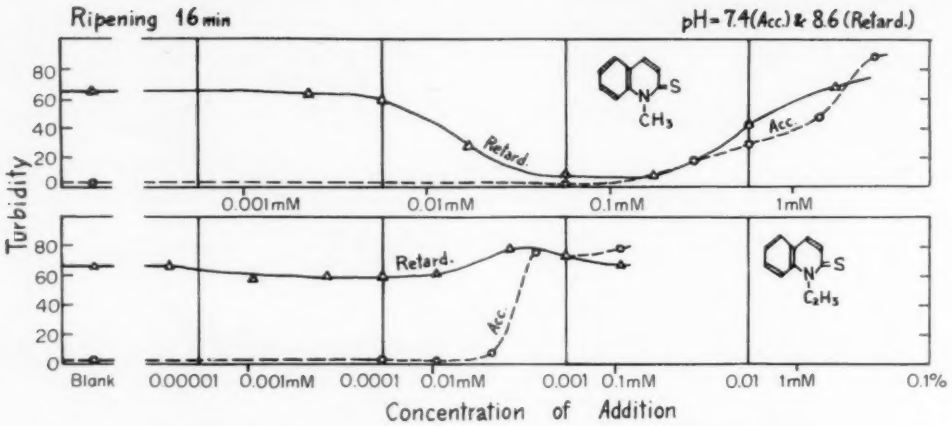

Fig. 3. Accelerating and retarding characteristics of N-methyl- and N-ethyl-quinoline-2-thione.

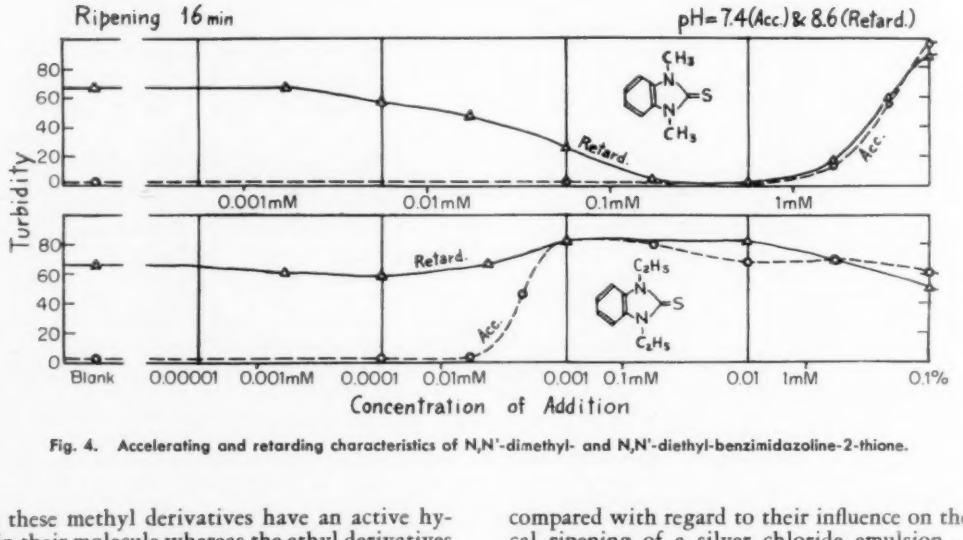

Fig. 4. Accelerating and retarding characteristics of N,N'-dimethyl- and N,N'-diethyl-benzimidazoline-2-thione.

that all these methyl derivatives have an active hydrogen in their molecule whereas the ethyl derivatives do not. It can be assumed that the retardative properties of some of the artificial retarders, such as thiol compounds (e.g. l-cysteine, thiouracil, 2-mercaptobenzothiazole) or imidazoles and triazoles,[7] are attributable to the presence of active hydrogen atoms in their molecules, although this assumption is not verified as yet.

Conclusion

The dual properties of 2-mercaptobenzothiazole as an accelerator and retarder of physical ripening of a silver chloride emulsion was demonstrated by the use of polyvinyl alcohol individually or together with polyvinyl pyrrolidone as protective colloid. Among the N-alkyl derivatives of this compound and related compounds, such as quinoline-2-thione or benzimidazoline-2-thione, the methyl and ethyl derivatives were compared with regard to their influence on the physical ripening of a silver chloride emulsion. It was found that all of the methyl derivatives of the above mentioned compounds are very active retarders while the ethyl derivatives, on the contrary, are very active accelerators of physical ripening.

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Measurement of the Ratio of Lateral to Vertical Dye Diffusion Rates in Swollen Gelatin Coatings

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Measurements of lateral and vertical diffusion rates of an acid dye at pH 4.2 and 20 C in two hardened gelatin coatings, one of which contained a mordant, are described. A technique of arresting diffusion by rapid freezing and low-temperature dehydration has been employed, and the penetration of the dye in the lateral and vertical directions has been measured in dry sections by means of a microdensitometer of special design. The results show that, for the particular cases studied, there are no significant differences in the diffusion rates in the lateral and vertical directions.

The transfer of dye from a matrix into a mordant blank in imbibition printing proceeds initially in the vertical direction, that is, in the direction perpendicular to the plane of the coating. The rate of vertical diffusion is of primary interest if one enquires what length of time a transfer will require. On the other hand, when questions of image sharpness or lack of sharpness due to lateral diffusion of a dye come into consideration, the rate of lateral diffusion is of importance. In practice, during transfer, diffusion in the mordant blank will occur simultaneously in the lateral and vertical directions at any edge of the image.

A question of technical interest is whether or not the lateral diffusion rate is greater than the vertical rate. A coated gelatin layer, upon drying, undergoes a dimensional change chiefly in the vertical direction, which usually results in a structural anisotropy. Arguments can therefore be advanced for the view that the lateral and vertical diffusion rates in swollen coatings should be different, but the question can only be decided by experimental measurements.

A measurement of the ratio was made in 1949 by Chmutov and Bromberg[1] and the conclusion was reached that no significant difference exists between the lateral and vertical diffusion coefficients. We have confirmed this result in a series of independent measurements by a different method with the dye, Brilliant Alizarine Light Red B, and with two hardened gelatin coatings, one of which contained a cationic organic mordant.

Method

The method of measuring diffusion was the same as that described by Jelley and Pontius[2] for measuring the diffusion of dyes in gelatin on a microscopic scale. This was essentially a process of dyeing a gelatin coating for a definite time, arresting diffusion by rapidly freezing the sample in a low-temperature bath of alcohol and solid carbon dioxide, and drying the sample by means of a sweep gas of dry nitrogen precooled below —6 C. The dry samples were sectioned in a microtome and the penetration of the dye was measured by scanning the section with a special microdensitometer.

The microdensitometer, which was described previously,[2] was so arranged that an image of an illuminated slit was projected onto the 5-μ-thick section. The geometrical image of the slit, in the section scanned, was 2.1 μ long and 0.2 μ wide, although, owing to diffraction, the effective width was between 0.5 and 1.0 μ. Instead of moving the section during scanning, the light source was moved on a micrometer screw, the section remaining stationary, and the light transmitted by the section was allowed to fall on a photomultiplier tube. By means of calibration densities and a recorder, the density of the dye in the section could be recorded automatically as a function of distance from the front surface of the coating.

In order for the comparison between vertical and lateral diffusion to be as free from error as possible, it was desirable that both modes of diffusion take place simultaneously in the same sample of coating and in such a manner that each mode occurred without admixture with the other. The method was accordingly modified in the following manner:

If a small sample with a sharply cut edge were immersed in a dye bath, diffusion into the gelatin, vertically through the surface and laterally through the edge, would take place. However, in order to separate the two modes of diffusion, an impermeable layer over the surface at the edge would be required.

The arrangements shown in Fig. 1 were used. A small sample of coating, about 35 × 50 mm, was carefully covered on about one half the coated side by waterproof adhesive tape. The tape was

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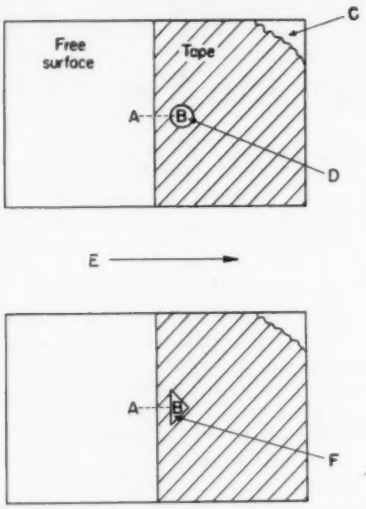

Fig. 1. Method of taping the sample. A-B, traverse of microtome in sectioning; C, loose edge of tape; D, $^1/_4$-inch-diameter punched hole; E, longitudinal direction of coating; F, razor-blade-cut edge.

left loose over one corner so that later, after dyeing and just before freezing, it could be quickly removed. About $^1/_{16}$ in. from the inner edge of the tape, a hole $^1/_4$ in. in diameter (D) was punched with a specially machined steel punch (Fig. 1, top). The sharp edge could also be made with a new razor blade, cutting as shown in F (Fig. 1, bottom).

Later on, after dyeing, freezing, and drying, a section was cut by microtome from A to B. In a single section, therefore, pure vertical diffusion (A) and pure lateral diffusion (B) could be seen. Photomicrographs of two parts of a typical section are reproduced in Fig. 2.

Dyeing, Freezing, Drying

The taped and punched sample was placed in a buffer bath of the same pH as the dye bath and at the same temperature for 10 min to allow the gelatin to swell to equilibrium. It was then immersed in the dye bath where the free surface of the sample and edges of the punched hole were brushed over about two times a second by a rotating camel's-hair brush turning within the dye bath. At the end of the dyeing period, from 49 to 289 sec, the tape was

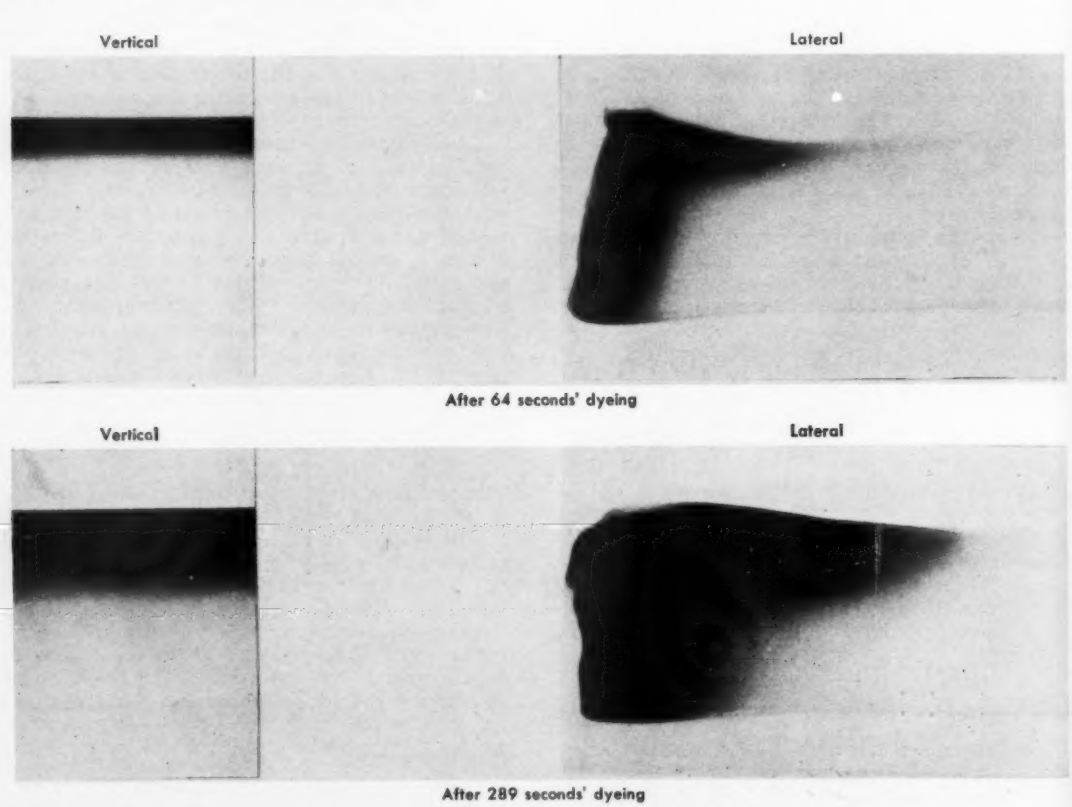

Fig. 2. Photomicrographs of thin sections, showing vertical and lateral diffusion in a gelatin coating containing hardener and mordant. Lateral diffusion is seen to be contaminated by vertical diffusion at top of sections. Measurements of lateral penetration would be made at lower portion next to the support.

torn off and the whole sample plunged into the freezing mixture of alcohol and Dry Ice. The sample was then clamped quickly in the drying apparatus in which a jet of cold, dry nitrogen passed over the gelatin, which dried below the freezing point of water in a period of less than 20 min.

Materials

The coatings used were hardened, clear gel coatings on ciné positive support. The dye bath was prepared with 0.3 gram per liter of purified Brilliant Alizarine Light Red B, buffered with sodium citrate, sodium acetate, and acetic acid to a pH of 4.2. The buffer bath presoak was exactly the same as the dye bath but without the dye. Swelling in the buffer bath and dyeing were done at 20 C.

Defects of the Method

Two serious criticisms of the experimental method are (1) that incomplete sealing at the edge by the adhesive tape can permit some lateral swelling of the gelatin and (2) incomplete sealing can also permit vertical diffusion at the edge. Both defects occurred frequently so that about half of all the samples prepared had to be rejected. It was also necessary to exclude unhardened coatings and confine the work to hardened coatings, which show a much smaller degree of swelling.

Substitutes for adhesive tape, such as collodion, were tried unsuccessfully. The main reason, however, for not employing such a substitute for adhesive tape was that the sealing layer has to be removed as fast as possible just after dyeing and before freezing, since it could not be removed after freezing and before drying.

Thickness Measurements

The microdensitometer measurements must be made on sections cut in the dry samples. Actual diffusion takes place when the samples are swollen to the equilibrium value at the pH and temperature of the dye bath. The penetration distances measured must be converted to the value they would have if the measurements were made on the swollen material. In the lateral direction, essentially no swelling takes place, but a correction for swelling must be made on the vertical penetration measurements.

The thickness of the swollen gelatin layer was determined by micrometer measurements on a large number of samples and obtained by the difference between the swollen coating and the thickness of the support alone. The dry thickness was found in a similar manner.

In making the measurements of swollen thickness, the samples, about 35 mm square, were first soaked for 10 min in the buffer bath at pH 4.2 and 20 C. The samples were removed, two at a time, pressed for a second against a filter paper which had been dampened with the buffer, placed together face to face, and the total thickness was measured in five places with a micrometer. Ten to twelve pairs of samples constituted one set, and four such sets of measurements on each coating, dry and swollen, were made. The dry and swollen thicknesses of the support alone were determined similarly. The thicknesses were also confirmed by direct measurements of sections with the microscope. The results are shown in Table I.

TABLE I

Measurement of Swollen Thickness and Swelling Ratio, pH 4.2, 20 C

Coating Containing Hardener and Mordant	
Swollen thickness	$30.15 \pm 0.89\ \mu$
Dry thickness	$14.46 \pm 0.15\ \mu$
Swelling ratio	2.08 ± 0.065
Coating Containing Hardener Only	
Swollen thickness	$31.64 \pm 0.64\ \mu$
Dry thickness	$12.89 \pm 0.21\ \mu$
Swelling ratio	2.46 ± 0.064

Measurement of Diffusion Coefficients

An examination of sections under the microscope made possible the rejection of those in which the experimental conditions of dyeing had been unsatisfactory. That is, those sections of samples in which the lateral diffusion was complicated by admixture with vertical diffusion due to poor sealing at the edge were discarded. The remaining sections were scanned vertically and laterally with the microdensitometer. Since both modes of diffusion are present in different positions of a single section, the section thickness and therefore the maximum density is the same for both scans. The lateral scan was made close to the support so as to be well away from any vertical diffusion which might have been present due to leakage from the sealed surface. Reproductions of representative microdensitometer traces are shown in Figs. 3 and 4. The broken lines in the figures represent arbitrary extrapolations to the density at zero diffusion time.

Computation of Results

The rate of diffusion depends upon the concentration gradient, which, in turn, depends upon the depth to which diffusion has proceeded. It is therefore customary to characterize the rate of diffusion by a coefficient D defined as the coefficient in Fick's law, expressed by the equation,

$$\frac{\partial c}{\partial t} = \frac{\partial}{\partial x}\left(D\frac{\partial c}{\partial x}\right), \qquad (1)$$

where c may be taken here to represent the concentration of both free and adsorbed dye within the gelatin at time t, and at any point x, counted as positive, inward from the surface. Although the diffusion coefficient D is frequently itself a function of concentration, for many purposes it can be assumed to be a constant, to a good approximation, in which case the diffusion equation can be readily solved[3] to give

TABLE II

Vertical and Lateral Diffusion Data for Coating Containing Hardener and Mordant

Time t in Seconds and Dry Penetration Distances x and y in Microns

t	x	$\frac{x}{\sqrt{t}}$	y	$\frac{y}{\sqrt{t}}$
64	2.66	0.332	5.70	0.713
81	2.82	0.313	5.98	0.665
121	2.94	0.267	7.88	0.716
144	3.58	0.298	7.01	0.585
169	3.58	0.275	7.50	0.576
196	3.91	0.279	8.21	0.586
289	5.05	0.297	9.24	0.542

Average value of $\frac{x}{\sqrt{t}}$ is $(0.294 \pm .021) \times 10^{-4}$ cm sec$^{-\frac{1}{2}}$.

Average value of $\frac{y}{\sqrt{t}}$ is $(0.626 \pm .066) \times 10^{-4}$ cm sec$^{-\frac{1}{2}}$.

$$\frac{c}{c_0} = 1 - \frac{2}{\sqrt{\pi}} \int_0^{\frac{x}{2\sqrt{Dt}}} e^{-\beta^2} d\beta, \tag{2}$$

where c_0 is the concentration of dye at the surface of the gelatin layer, and β is the parameter in the error function. It is clear that if the ratio of c/c_0 at position x and time t is known, the value of D can be calculated. If one evaluates Eq. (2) for the case where $\frac{c}{c_0} = \frac{1}{2}$, the diffusion coefficient is given by

$$D = \left(\frac{x}{\sqrt{t}}\right)^2 \Big/ 0.910. \tag{3}$$

In practice, samples were dyed for a number of different times in a dye bath of sufficient volume so that the concentration in the dye bath could be considered constant. Under these conditions, the value of $x/\sqrt{t}$ should be a constant, and from the average of the values of $x/\sqrt{t}$, the diffusion coefficient could be calculated. In the present case, however, the ratio of lateral to vertical diffusion coefficient is required, so that we only need to evaluate the ratio of $(x/\sqrt{t})^2$ for lateral and vertical diffusion. Furthermore, it is not significant that the choice of penetration distance be the point where $\frac{c}{c_0} = \frac{1}{2}$ so long as the same value of $\frac{c}{c_0}$ is selected for both lateral and vertical cases.

Let x be the dry (measured) penetration distance for vertical diffusion and p the ratio of swollen to dry thickness. Let X be the vertical penetration distance in the swollen sample. Then

$$X = xp. \tag{4}$$

Similarly, let y be the dry measured penetration distance for lateral diffusion and q the ratio of wet to dry elongation, which, as far as can be determined, is within 1% of being unity. Let Y be the lateral penetration distance in the swollen sample. Then

TABLE III

Vertical and Lateral Diffusion Data for Coating Containing Hardener Only

Time t in Seconds and Dry Penetration Distances x and y in Microns

t	x	$\frac{x}{\sqrt{t}}$	y	$\frac{y}{\sqrt{t}}$
49	2.34	0.334	5.29	0.755
64	2.42	0.303	5.13	0.642
64	2.01	0.251	4.40	0.550
81	3.04	0.338	5.73	0.637
81	2.26	0.251	5.75	0.640
100	2.88	0.288	8.25	0.825
100	2.01	0.201	4.40	0.440
121	3.32	0.301	9.90	0.899
144	4.29	0.357	8.12	0.676
169	3.64	0.280	12.34	0.950
169	3.74	0.288	10.50	0.808
196	3.82	0.273	9.86	0.704

Average value of $\frac{x}{\sqrt{t}}$ is $(0.289 \pm .027) \times 10^{-4}$ cm sec$^{-\frac{1}{2}}$.

Average value of $\frac{y}{\sqrt{t}}$ is $(0.711 \pm .092) \times 10^{-4}$ cm sec$^{-\frac{1}{2}}$.

$$Y = yq \cong y \tag{5}$$

and

$$\frac{D_L}{D_V} = \frac{\left(\frac{Y}{\sqrt{t}}\right)^2}{\left(\frac{X}{\sqrt{t}}\right)^2} = \frac{\left(\frac{y}{\sqrt{t}} \cdot 1\right)^2}{\left(\frac{x}{\sqrt{t}} \cdot p\right)^2}. \tag{6}$$

The values of $\frac{x}{\sqrt{t}}$ and $\frac{y}{\sqrt{t}}$ are shown in Tables II and III.

The ratios of lateral to vertical diffusion coefficients are found by substituting the values of swelling ratio from Table I and the values of $\frac{x}{\sqrt{t}}$ and $\frac{y}{\sqrt{t}}$ from Tables II and III into Eq. (6). For the coating containing hardener and mordant, we obtain

$$\frac{D_L}{D_V} = \frac{[(0.626 \pm .066)\ (10^{-4})]^2}{[(0.294 \pm .021)\ (10^{-4})\ (2.08 \pm .065)]^2} \tag{7}$$

and

$$D_L/D_V = 1.04 \pm 0.18. \tag{8}$$

Also, for the coating containing hardener only,

$$\frac{D_L}{D_V} = \frac{[(0.711 \pm .092)\ (10^{-4})]^2}{[(0.289 \pm .027)\ (10^{-4})\ (2.46 \pm .064)]^2} \tag{9}$$

and

$$D_L/D_V = 1.00 \pm 0.23. \tag{10}$$

The approximate absolute values of the diffusion coefficients can be found by use of Eq. (3). The vertical diffusion coefficient in the coating containing hardener and mordant is $0.41 \pm 0.05 \times 10^{-8}$ cm^2 sec^{-1} and in the coating containing hardener only, the

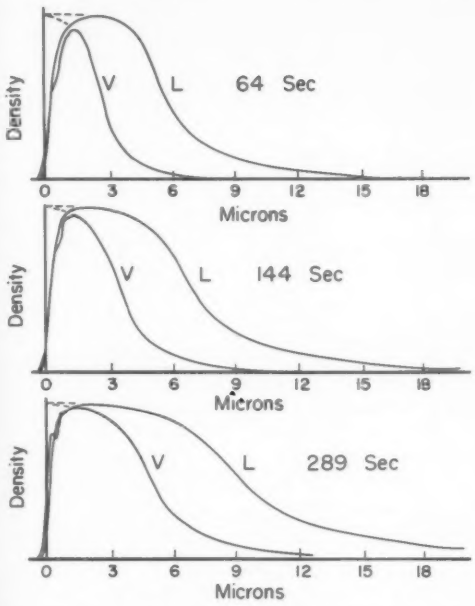

Fig. 3. Microdensitometer traces of dye in sections of coating containing hardener and mordant, showing: V, vertical diffusion; L, lateral diffusion. Density is proportional to dye concentration.

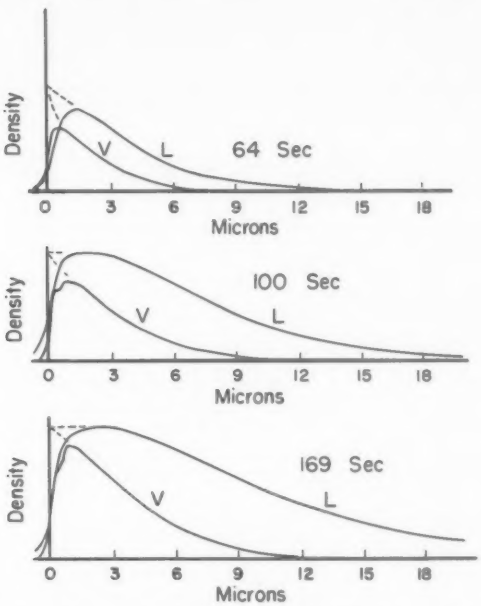

Fig. 4. Microdensitometer traces of dye in sections of coating containing hardener only, showing: V, vertical diffusion; L, lateral diffusion. Concentration gradient is lower than that when mordant is present.

vertical diffusion coefficient is $0.55 \pm 0.08 \times 10^{-8}$ cm^2 sec^{-1}.

The ratios of lateral to vertical diffusion coefficients are close to unity for both coatings used. In both cases, the probable error is of the order of 20%. The large magnitude of the probable error reflects the difficulty of measuring on the microscopic scale as well as the compounding of the separate errors of diffusion measurement and swelling measurement. Within the limits of the experimental error, however, it can be said that there is actually no significant difference between the dye diffusion coefficients in the lateral and vertical directions (for the cases examined).

Conclusion

The result which has been obtained in the present experiments, namely, that no significant difference in the lateral and vertical diffusion rates has been detected, is contrary to the result to be expected if the structural anisotropy of the dry coating due to constrained drying persists in the swollen coating. It is, of course, not excluded that small differences actually do exist, but any large difference in lateral and vertical diffusion rates under the conditions of the experiment is unlikely.

Diffusion is a random molecular process. A single molecule which diffuses forward will experience random deflections in all directions owing to encounters with the protein, water, mordant, and dye molecules. The existence of a concentration gradient means the diffusing dye molecule will encounter more dye molecules in the backward than in the forward direction. During two-thirds of the time, the molecule will have components of velocity along the axes mutually perpendicular to that of the concentration gradient, so that, on the whole, a diffusing molecule samples its surroundings isotropically. It may be concluded, therefore, that the diffusion measurements do not give evidence of significant anisotropy of the swollen gelatin.

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Combined Development and Fixation of Photographic Images with Monobaths

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A combined developing and fixing bath is described that retains, to a marked degree, the sensitometric characteristics of conventionally developed film and paper. An evaluation of the system is made, based on changes in formulation and processing conditions. The utilization of the monobath as a high-speed developer is also discussed.

Since 1889, investigators in the field of photography have been experimenting with solutions which would permit the simultaneous development and fixation of films and papers. The advantages of such a system are obvious. The elimination of separate baths for developer, hardener, and fixer minimizes space requirements and permits the design of small, compact processing equipment. In addition, the processing requirements of one-bath systems are not stringent since variations in the degree of agitation and time of development do not have an appreciable effect on the characteristics of the image. The intensification of developer activity caused by agitation is approximately compensated for by an increase in the rate of fixation. Since development is automatically arrested by the action of the hypo, there is no need for precise timing of development.

Monobaths, as they are usually called, were not widely adopted in the past because of serious shortcomings that were believed to be inherent in the nature of the system. Such stumbling blocks as loss of emulsion speed, high fog, poor contrast, reticulation, unevenness of development, poor keeping qualities, and rapid exhaustion relegated monobaths to the laboratory notebooks along with the rest of the myriad of photographic curiosities.[1] Today, however, with the urgent requirement for compact, rapid photographic processors for in-flight processing in drone and manned aircraft, evaluation of missile guidance systems, recording of cathode-ray display, time-lapse photography, data recording, etc., there has been renewed interest in the development of a workable monobath system. As a result of intensive investigations by several manufacturers and research institutes, commercial systems have been devised which produce in many respects approximately the results obtained with conventional processing. Since most of these systems leave much to be desired, it was the purpose of this investigation to develop a monobath that would retain all the sensitometric characteristics of conventionaly processed film and paper.

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Problems Involved in Formulating Monobaths

The problem of emulsion speed retention has been the Achilles' heel of most monobath formulations. It can easily be seen that an extremely active developer having a very short induction period must be used so that exposed silver halide grains can be developed before they are attacked by the hypo and dissolved. Most successful monobaths are based on this premise. But formulating with this goal in mind is complicated by the fact that the components of a monobath are all interdependent. The manipulation of the developer to yield increased activity brings with it other problems—for example, high fog, reticulation, and rapid exhaustion—that are difficult to correct without again destroying the activity of the developer.

Most of the monobaths reported on in the literature are based on a Metol–hydroquinone formulation with a large percentage of sodium hydroxide accelerator. Good results with a monobath of this type have been achieved at Boston University.[2] BU Monobath 315, for example, has the formulation shown in Table I.*

Research workers at Boston University have solved many of the problems associated with monobaths, but some loss in emulsion speed is still evident, and increased exposure is required to give results comparable to conventional processing.

Monobath Formulation for Film

Recent articles in the literature have indicated the effectiveness of Phenidone (1-phenyl 3-pyrazolidone)

* The following article by H. S. Keelan of Boston University, which describes the use of Phenidone in monobaths, appeared after this manuscript was completed: H. S. Keelan, "Simultaneous Developing and Fixing of Photographic Images," *J. Phot. Sci.*, 5: 144–6 (Nov.–Dec. 1957).

as an accelerator for weak developing agents.[3] We have also determined that the addition of small quantities of Phenidone to conventional developers results, in many cases, in an increase of effective film speed. It was felt, therefore, that the substitution of Phenidone for Metol in a monobath formulation might result in improved developer activity. Preliminary tests indicated the efficacy of this system, and subsequent work was based entirely on Phenidone–hydroquinone formulations.

Since the developer portion of this formulation proved to be exceedingly active, we were able to increase the amount of hypo in the formulation to 250 grams/liter without deleterious effect on film speed or maximum density. Although it is commonly known that the incorporation of small percentages of hypo in a developer causes fogging, it was found that, at higher concentrations, the hypo acts to some extent as an antifoggant. We were thus able to eliminate from the formulation all antifoggants which normally cause a reduction in film speed, as for example, benzotriazole, potassium bromide, etc. Resultant fog density was in most cases about 0.1 above that of conventional developer.

Comparisons with ASA developer indicated no loss in film speed for representative films tested, e.g., Eastman Tri-X Panchromatic Negative Safety Film, Type 5233 (35mm) Exposure Index 320; Kodak Super-XX Aerial Recon. Reconnaissance Base Film, Exposure Index 100; Kodak Tri-X Aerial Recon. Reconnaissance Base Film, Exposure Index 200. For these tests, a monobath formulation was selected which produced the same gamma at 68 F as that obtained from standard ASA developer.

TABLE I
BU Monobath 315

Water	750 cc
Metol	10 grams
Sodium sulfite	50 grams
Hydroquinone	40 grams
Potassium alum	20 grams
Sodium hydroxide	35 grams
Hypo	110 grams
Kodak Antifog #2 (0.5% soln.) (6-nitrobenzimidazole nitrate)	20 cc
Water to make	1000 cc

TABLE II
USASEL Monobath 24-2

Water (90–100 F)	750 cc
Sodium sulfite (anhydrous)	60 grams
Hydroquinone	30 grams
Sodium hydroxide	25 grams
Phenidone	0.8–5.0 grams
Sodium thiosulfate (crystal)	75–250 grams
Ice water to make	1000 cc
Formaldehyde (38%)	10 cc

Note: Although not essential, ice water was used to cool the solution rapidly before the addition of the formaldehyde, thus preventing excessive oxidation. The pH of this solution is approximately 10-11.

Excessive softening and uneven development were troublesome factors and the use of some type of film hardener was indicated. Potassium alum, although effective as a buffer to maintain uniform pH, is not a useful hardener in the presence of sulfite at high pH.[4] Formaldehyde, on the other hand, has the dual function of developer and hardener in basic solution. It was used successfully in our monobath, to prevent reticulation and provide for maximum density.

After several modifications, the basic formulation for our monobath was as shown in Table II. The ingredients were dissolved in the order given in the table. Good results were also obtained when the solid ingredients were added as one package to a warm mixture of water and sodium hydroxide.

It was found that there is no apparent difference in the characteristic curves of films processed in formulations containing 0.8–5.0 grams of Phenidone. In order to minimize exhaustion of developer, we used 3 grams of Phenidone in our experimental formulations.

Monobath Formulation for Paper Processing

The monobath discussed in the previous section was unsuitable for paper processing because of the development of excessive fog in the unexposed areas. We were able to overcome this difficulty, however, by the use of antifoggants in the monobath formulation. Excellent results were obtained with waterproof, high-speed, variable contrast paper, but standard silver bromide enlarging papers developed brown images of extremely poor density and contrast.

The formulation developed for use with waterproof paper is shown in Table III:

TABLE III
USASEL Monobath 24-2D

Water (100 F)	750 cc
Sodium sulfite (anhydrous)	60 grams
Hydroquinone	30 grams
Sodium hydroxide	25 grams
Phenidone	3 grams
Potassium bromide	2 grams
Benzotriazole	4 grams
Sodium thiosulfate (crystal)	150 grams
Water to make	1000 cc
Formaldehyde (38%)	10 cc

Experimental Procedure

Films 35mm wide were cut into 10-in. strips and exposed in the Eastman Sensitometer, Type IIb (color temperature 5400 K). Processing was accomplished in a tray with constant agitation, using an 8 × 10-in. plastic holder capable of holding five strips of film.

Comparison of Phenidone, Metol Monobaths

The superiority of Phenidone over Metol as an activator for hydroquinone in a monobath is shown in Fig. 1. The Phenidone monobath was prepared

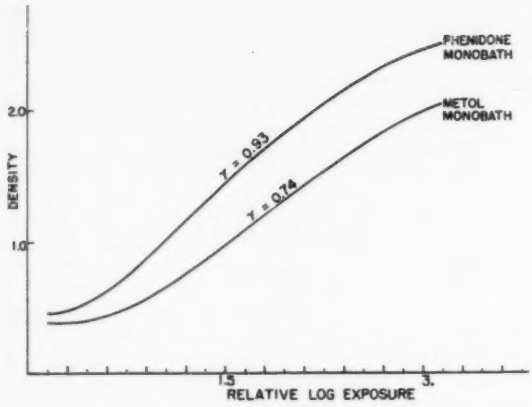

Fig. 1. Comparison of Phenidone and Metol monobaths; Eastman Tri-X Panchromatic Negative Safety Film, Type 5233 (35mm), tray processed at 68 F for 3 min.

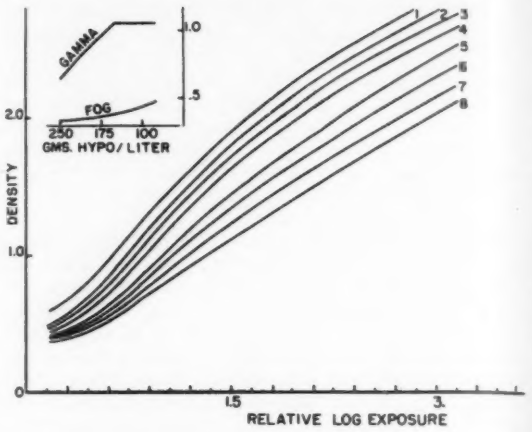

Fig. 2. Effect of hypo variation on monobath; Eastman Tri-X Film (35mm), tray processed at 68 F.

Curve No.	Grams of hypo per liter	Processing times, min at 68 F
1	75	4
2	100	3½
3	125	3¼
4	150	3
5	175	2¾
6	200	2½
7	225	2¼
8	250	2

according to the standard formulation given for film, using 150 grams/liter of sodium thiosulfate. The Metol monobath was made with the same formulation, except that 10 grams of Metol were substituted for the 3 grams of Phenidone. It can be seen from the characteristic curves that the Phenidone system results in a marked increase in speed, contrast, and maximum density.

Effect of Hypo Variation on Sensitometric Characteristics of Film Developed in Monobath

Normally, the gamma value of a specific monobath solution is fixed, and cannot be varied appreciably by change in dilution or time of development. Temperature changes have some effect, and will be discussed in the next section. This inflexibility greatly limits the processing latitude offered by monobaths. It is possible, however, to obtain a wide gamma range without forfeiting film speed by using the rather simple expedient of variation in hypo content. Figure 2 shows the effect of hypo variation on the characteristic curves of Tri-X 35mm film, developed in USASEL Monobath 24-2. A gamma range of 0.65–1.05 is obtained within the hypo range of 250–150 grams/liter of solution. This compares favorably with the curves shown in Fig. 3, which illustrates the family of characteristic curves of Tri-X 35mm film conventionally developed in Kodak Developer D-76 for 6–20 min.

A set of gamma vs. hypo concentration curves can be derived for individual films, which are similar to the development time vs. gamma curves used in standard processing. Figure 4 shows a typical set of characteristic curves for Tri-X Aerial Recon. Film. The range here for gamma is 0.75–1.25 for a corresponding range of 75–225 grams of hypo per liter of solution. Similar investigations with Super-XX Aerial Recon. Film resulted in a gamma range of 0.65–1.50 for a hypo content of 100–250 grams/liter.

When rapid fixation is necessary, high temperature processing and concentrations of 250 or 200 grams of hypo per liter are recommended. Complete processing times of from 10 sec to 4 min, depending on the film, can be achieved by variation in hypo and temperature.

Effect of Temperature Variation on USASEL Monobath

The reciprocal balance between the activity of the developing and fixing components of the monobath system is distinctly altered by variation in processing temperature. At low temperatures, the activity of the developer is not sufficient to overcome the action of the hypo so that film speed, gamma, and fog are reduced. At higher temperatures, developer activity increases, but since there is not a proportional increase in the rate of fixation, film speed, gamma, and fog level continue to rise. This change is represented by Fig. 5. For this experiment, USASEL Monobath 24-2, containing 150 grams of hypo per liter, was selected to process Tri-X Aerial Recon. Film. Film speed was taken as the log exposure required to produce a density equal to gamma. Similar characteristic curves were obtained with Tri-X 35mm Film and Super-XX Aerial Recon. Film. The effectiveness of the hardening action of formaldehyde can be seen in the comparatively low fog level developed by the Tri-X Aerial Recon., an unhardened film, at 110 F.

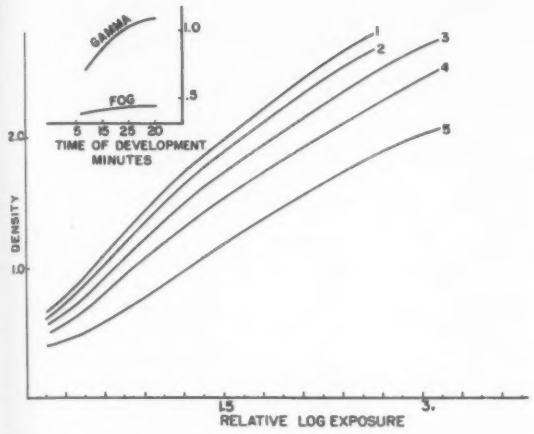

Fig. 3. Characteristic curves of Eastman Tri-X Film (35mm) developed in Kodak Developer D-76.

Curve No.	Min at 68 F
1	20
2	15
3	12
4	10
5	6

Characteristics of Monobath Used as a High-Speed Developer

An analysis of the degree of development of films processed in USASEL Monobath 24-2 at 10-sec time intervals was undertaken in order to determine its efficiency as a high-speed developer. Even though test conditions for such short development times precluded exact reproducibility of data, the superior activity of the monobath system over conventional developers was apparent in all cases.

A comparison of the monobath system with the following conventional rapid developers was made: Ethol-90, Kodak DK-60A, Ilford ID-62, and Kodak D-72. Developers were used undiluted in all tests. In the absence of specialized high-speed processing equipment, it was desirable to keep the activity of the system low enough to allow for reasonably accurate determinations. For this purpose, a monobath containing 150 grams of hypo per liter and processing temperatures not higher than 85 F were chosen. For extended activity, reduced hypo and increased temperature are recommended. Test strips of Tri-X 35mm film were exposed in the IIB Sensitometer and placed in an 8 × 10-in. plastic holder which held five strips of film in a tray. Strips were removed at 10-sec intervals, placed immediately in stop bath, and then fixed in Kodak Acid Fixer.

Typical results are shown in Fig. 6, which compares the developer activity of Ethol-90 and Monobath 24-2 at 68 F. The gradual increase in gamma and speed exhibited by the Ethol-90 is characteristic of the conventional developers examined. Monobath 24-2, on the other hand, develops to almost maximum

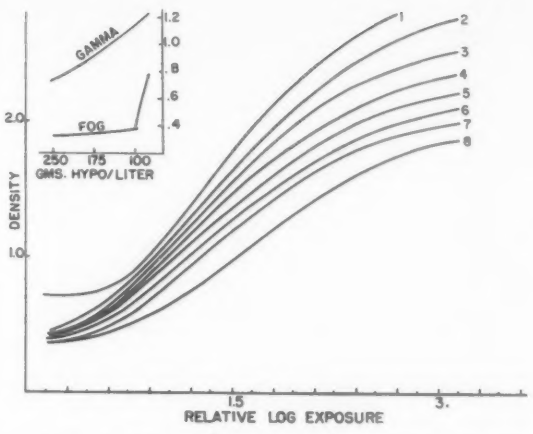

Fig. 4. Effect of hypo variation on monobath; Kodak Tri-X Aerial Recon. Film, tray processed at 68 F.

Curve No.	Grams of hypo per liter	Processing times, min at 68 F
1	75	4
2	100	3 1/2
3	125	3 1/4
4	150	3
5	175	2 3/4
6	200	2 1/2
7	225	2 1/4
8	250	2

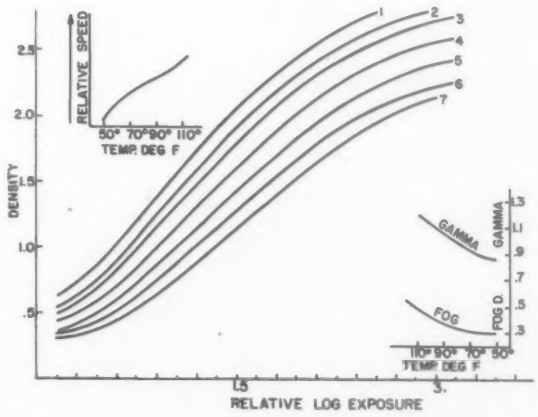

Fig. 5. Effect of temperature variation on monobath; Kodak Tri-X Aerial Recon. Film, tray processed.

Curve No.	Processing Times, min	Temperature, deg F
1	1	110
2	1 1/2	100
3	2	90
4	2 1/2	80
5	3	70
6	3 1/2	60
7	4	50

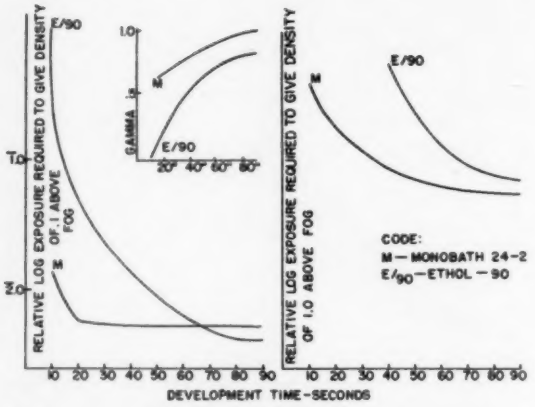

Fig. 6. Characteristics of USASEL Monobath 24-2 and Ethol-90 used as high-speed developers. Eastman Tri-X Film (35mm), tray processed at 68 F.

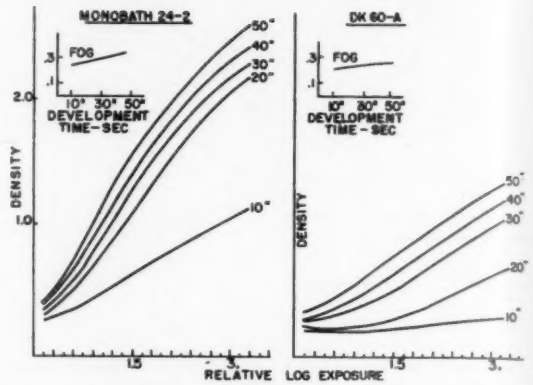

Fig. 7. Developer activity; USASEL Monobath 24-2 vs. Kodak Developer DK-60A; Eastman Tri-X Film (35mm), tray processed at 85 F.

speed and useful gamma after 20 sec of processing at 68 F. An even more rapid climb to maximum speed and gamma occurs when the processing is carried out at a higher temperature. This is shown in Fig. 7. The characteristic curve obtained after 40 sec development in DK-60A at 85 F is duplicated by only 10 sec of processing in monobath developer.

Since the processing time of most monobath systems is restricted by the rapidity with which the film can be cleared, a two-bath system, utilizing a high-speed developer, such as we have described, and a rapid fixing solution, such as ammonium thiocyanate, might be expeditious for ultra-rapid processing at moderate temperatures.[5]

Keeping Quality and Useful Capacity of USASEL Monobath

Airtight bottles of unused monobath solutions were stored for one year with no apparent discoloration or deterioration. Characteristic curves of film strips developed in the aged monobath were equivalent to those made with fresh solution.

If aerial oxidation is avoided, the useful capacity of this solution is excellent. Four-hundred feet of fully exposed 35mm film, Dupont 931, were processed in *1 qt* of USASEL Monobath 24-2, containing 250 grams of hypo per liter, in a deep tank at 90 F without loss of speed or reduction in gamma or maximum density. This is equivalent to processing 80 sheets of 8 × 10-in. film. The normal useful capacity for D-19 as given by Eastman Kodak is 60 sheets of 8 × 10-in. film processed at 68 F in *1 gal* of solution.

The monobath system seems to offer somewhat of an automatic internal compensating device. As we have shown in the previous section on hypo variation, reduction in hypo content results in increased gamma and maximum density. It would appear, therefore, that the exhaustion of developer is counterbalanced by a corresponding reduction in hypo content, thus maintaining the developer/hypo activity ratio of the fresh solution. The original formulation, therefore, acts as a suitable replenisher for the system.

Image Stability on Storage

There was no evidence of staining, fading, or yellowing when unwashed film and paper strips which had been developed in monobath and neutralized in a stagnant rinse of 2% acetic acid solution were stored in a drawer at room temperature for one year.

Acknowledgments

The author is indebted to K. Leistner, Consultant to the Photo Branch, USASEL, for his invaluable encouragement and technical advice.

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Projection of Photographic Data Recording Two-Tenths Second After Exposure

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Equipment and processing solutions are described which permit the photographing, processing, and projection in 0.2 sec of data obtained on a plan-position indicator. The equipment is designed to use two-solution processing, which gives results superior to those obtained with monobath processing

A number of systems have been designed for obtaining pertinent information from a cathode-ray tube presentation; of these, the photographic technique has been of great value, especially in applications where the phenomena to be studied are of very short duration. The U.S. Army Signal Corps has employed this technique in one of the radar installations where the operation requires observing data obtained on a PPI (Plan-Position Indicator), subsequent screening of this information, and finally presenting it to a command group which interprets its tactical value.

The equipment, which is shown schematically in Fig. 1, takes a photograph of the PPI presentation at every scan of the radar antenna. After the film is automatically processed, the presentation is projected on a 5-ft diameter plotting board screen. Here, a number of observers plot on the surface of the plastic plotting board with a special grease pencil the targets observed. A second camera, which is integral with the first, takes the photographs of the plotting marks. These marks and any other notations are then projected on a 12-ft surveillance screen where the image is viewed by tactical personnel.

The successful operation of the installation depends, among other factors, on the speed with which the images are projected on the respective screens and on the quality of the image obtainable.

Conventional photography was first employed to obtain these results. The film was developed, fixed, washed, and dried, and then transported to the projection station. The technique, though satisfactory from the standpoint of quality, was considered unusable because of the long interval required between photographing the image and its projection. Other systems were employed in order to reduce this time interval; however, it was evident that the use of several solutions for processing the film would invariably result in a very long delay. Experiments carried out using single solutions indicated that film could be developed with a high energy developer and then dried and stabilized before projection. The film would not be cleared but would be projected through the undissolved silver halide. The Kenyon Company was successful in developing an equipment of this design which projects an image within 1.5 sec after exposure.[1,2]

In essence, the system consists of a developing chamber having a cavity of approximately 0.005 in. The 35mm film used for taking the photograph makes a seal with the lips of the chamber during the processing operation. The developing solution, which is preheated to 170 F, is sprayed on the film through a narrow slit located on the upper section of the chamber. The developer is withdrawn from a slit on the lower end by means of a vacuum produced by a self-contained pump. After development, which normally takes 0.6 sec, the film is kept in this chamber and hot air saturated with acetic acid vapor is drawn through the liquid ports. The hot air dries the film and the acetic acid vapor neutralizes the alkaline developing solution and stabilizes the image. The stabilization, however, is not complete and a yellow light is used for projection to prevent fading of the image. The drying and stabilizing operation takes a little less than 1 sec so that the image can be projected approximately 1.5 sec after exposure.

This system proved successful from the standpoint of speed of processing; however, it was found that the image contrast produced was low. The projection density (specular) of the special film used, which has a very thin, highly translucent emulsion, ranged from 1.66 to a maximum image density of 2.1. This low contrast, coupled with the very dense film base and the necessity of using yellow light, made it impossible to project the image enlarged to a screen size of 12 ft.[3]

In view of this, it was evident that a different technique had to be devised which could clear the film prior to projection. Monobath processing solutions were investigated. These solutions incorporate the developing and fixing agent in one formulation, and the chemistry is such that the developer acts before the fixer has a serious deteriorating effect on the latent image. Monobath

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Formerly the U.S. Army Signal Engineering Laboratories.

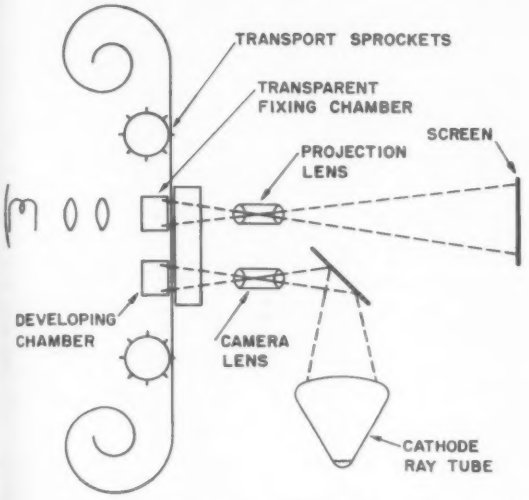

Fig. 1. Schematic diagram showing the optical system of the rapid processor.

solutions are well known in the literature. Due to the limited processing time requirements, however, new formulations had to be developed. These included compositions having concentrated reducing agents together with sodium thiosulfate or sodium thiocyanate as the fixing agent.

The formulation which gave best results is shown in Table I.

TABLE I

High-Speed Monobath Processing Solution

Water (125 F)	750 cc
Metol	12.9 grams
Sodium sulfite	70.9 grams
Hydroquinone	25.7 grams
Sodium hydroxide	25.7 grams
Benzotriazole	10.0 grams
Sodium thiosulfate	180.0 grams
Water to make	1 liter

This monobath gave excellent results at 140 F and 1.3 sec processing time. The film also showed very little of the base fog which is characteristic of monobath processing techniques. The image projected by using this system was satisfactory; however, a serious difficulty was encountered which made the technique impractical. The monobath solution forms a silver compound which precipitates and adheres to the surface of the developing chamber and its liquid ports. Since these ports are very narrow — approximately 0.005 in. wide — any foreign deposition causes restriction to the liquid flow sufficient to make the equipment inoperative after a very short time. Some monobath solutions caused difficulty in less than 20-min operation, while the formulation shown above gave satisfactory operation for a maximum of 2 hr.

It was evident, therefore, that the monobath technique could not be employed to its full advantage and a different method had to be used. Experiments had been conducted using the two-bath system which had shown promising results. This system involved the use of two chambers, one to develop the film, the other to clear it.

Space limitations and processing time requirements made it impractical to add an extra processing station between the developing chamber and the projection head. It was therefore decided to place the clearing station at the projection position. Figure 1 shows the relative position of the developing chamber and the transparent fixing chamber.

The fixing chamber consists of a stainless steel enclosure with a rubber seal facing the film and a glass plate opposite it. The liquid ports are located on the edge of the chamber. The clearing solution enters from the lower port and is exhausted from the upper section. Figure 2 shows the chamber.

The film is developed in the developing station and then transported to the transparent fixing chamber, or clearing station. Here the film makes a liquid seal with the rubber ring. The fixing solution is continuously circulated in the chamber to supply fresh liquid. The film is transported intermittently through the system and during this operation it is kept in constant contact with the ring seal of the fixing chamber. The internal pressure of the chamber is kept slightly lower than atmospheric in order to prevent liquid from leaking out in the event the seal is lost. Projection of the image is accomplished at this point, while the fixing solution is circulating in the chamber.

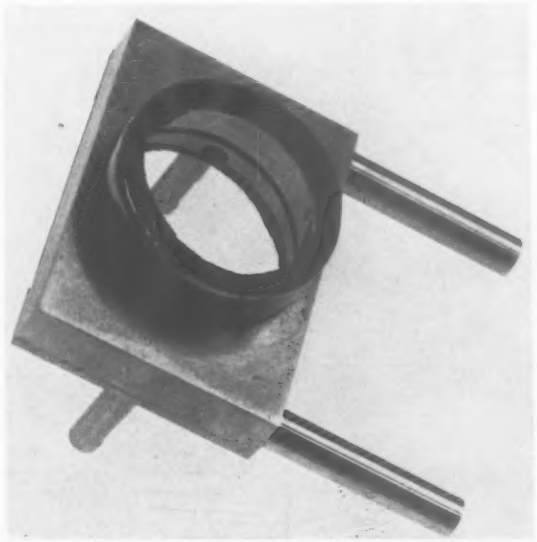

Fig. 2. Transparent fixing chamber used in the rapid processor, showing removable seal and liquid ports.

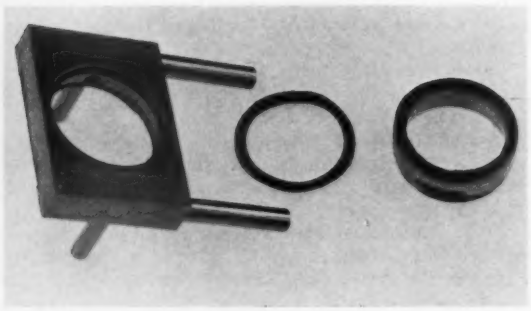

Fig. 3. Transparent fixing chamber, showing (left to right) chamber, ring seal, removable seal.

The transparent fixing chamber measures $1^1/_4 \times {}^{15}/_{16} \times {}^1/_2$ in. and has a cavity of approximately ${}^3/_4$-in. diameter $\times {}^7/_{16}$ in. deep. It is mounted to the projection head by a spring mechanism which produces a pressure against the film of approximately 4 oz. The rubber seal is enclosed on a stainless steel ring which screws onto the chamber proper thus allowing quick interchange of the seal without disturbing the chamber. Figure 3 shows a disassembled view. The chamber operates in a vertical position and is designed with a cone cavity having the larger section away from the film to allow the liquid to empty out completely when the equipment is stopped or upon interruption or the vacuum.

Figure 4 is a schematc representation of the general layout showing flow of the processing solutions. (Note that only one developing chamber and one fixing chamber are shown.) The drawing indicates a relatively large fixing solution supply which feeds the transparent chamber through a container kept at constant level. The level is maintained approximately 4 in. below the chamber to insure at this point a pressure lower than atmospheric. Liquid is drawn into the chamber by the vacuum pump and the waste liquid is emptied into a reservoir. A preheater heats the fixing solution to 205 F and maintains it at this value during the processing.

Extensive experiments were carried out to obtain developing and fixing solutions which would be suitable for this process. Fortunately, no work was required to obtain a new film, since the film already available for the single developer technique had the required characteristics for high temperature and fast processing methods.

Experiments conducted with the transparent fixing chamber indicated conclusively that the processing time could be reduced to a fraction of that required by the single developer system, because time for stabilizing and drying was no longer required. The formulations were directed, therefore, towards obtaining a developing time of the order of 0.4 sec. A formula was developed which surpassed this requirement and it was possible to process within 0.2 sec. The formulation used is shown in Table II.

TABLE II

Signal Corps High-Speed High-Temperature Developer

Water (60–70 F)	660 ml
Metol	13 grams
Sodium sulfite	80 grams
Hydroquinone	26 grams
Sodium hydroxide	26 grams
Benzotriazol (Kodak Antifog #1)	2 grams
Aerosol (10% soln.)	10 drops
Water to make	1 liter
Develop at 185 F for 0.2 sec	

The fixing solution performs two major functions. First, it must stabilize the silver halide to prevent fogging at the time the film is quickly transported from the developing chamber to the illuminated projection station; second, it must clear the emulsion in the shortest possible time. This is necessary since the uncleared film produces a very badly illuminated image on the screen. It was found that a clearing time of approximately 0.2 to 0.3 sec was necessary in order to be tolerable and compatible

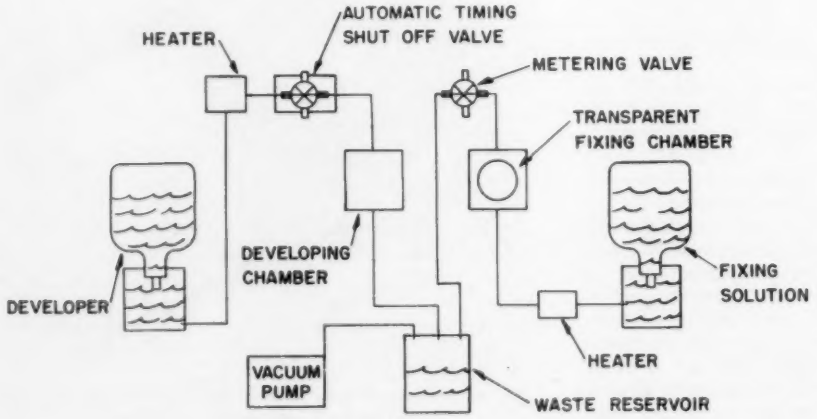

Fig. 4. Schematic diagram of the rapid processor, showing flow of processing solutions.

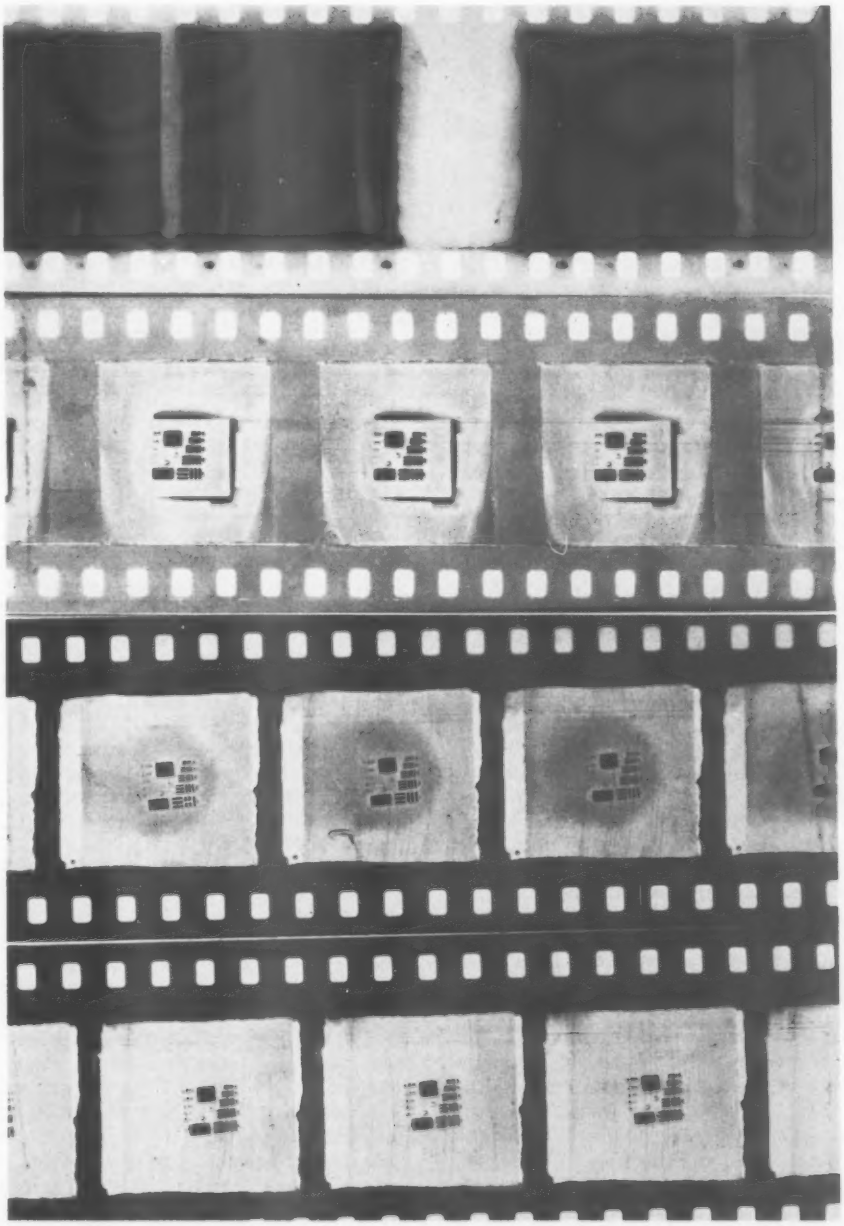

Fig. 5. Film densities resulting from different processing techniques. Reading from top to bottom: first film strip, single-step processed, stabilized with acetic acid vapors; second film strip, monobath processed; third film strip, two-bath processed in 0.4 sec; fourth film strip, two-bath processed in 0.2 sec.

with the transport time. The formulation best suited for this purpose is shown in Table III.

TABLE III

High-Speed Hot Clearing Solution

Hypo	500 grams
Aerosol	10 drops
Water to make	1 liter
Fix at 205 F	

No acid is added to the clearing solution for neutralizing the alkaline developer that remains on the film emulsion. It was found that at the high temperature used a slight acidity causes hypo to decompose and produce a sulfur precipitate which cannot be tolerated in this application. Temperature regulation is important since clearing activity varies considerably with changes in temperature. For instance, at 205 F the clearing time is 0.2 sec, at 200 F it is 0.4 sec, at 190 F it is 0.6 sec and at 180 F it is 1.0 sec. Hypo concentration is not as critical as temperature. Concentrations higher than 50% appear to cause no appreciable decrease in clearing time.

The film is not washed or rinsed during the process. Drying of the film is accomplished rapidly by exposure to ambient air. This is possible because the film emulsion is thin and absorbs very little water. Also, the film is wet only on one side and within a small area defined by the image size. Surface water is squeegeed by the rubber seal of the fixing chamber. Image stability under storage is very good. Samples have been kept over a year without noticeable stains, discolorations, or depreciation of the image quality.

The films used for this process are SO-1060, manufactured by Eastman Kodak Company, and Radarscope Film, Emulsion Type 450, manufactured by Ansco. Both films give satisfactory results; however, it has been found that the Ansco film produces a higher maximum density and can be cleared within a shorter time. Both films are orthochromatic, sensitive to blue, with an ASA speed of approximately 2 to 4. They have a fine grain structure which can resolve 150 lines/min. The emulsions have been prehardened to withstand high processing temperatures without employing additional hardening agents in the processing solutions.

Figure 5 shows representative samples of film strips obtained by some of the different techniques. Note the low contrast and heavy base fog of the first strip which was produced by developing the film and stabilizing it with acetic acid vapors. The second strip shows results obtained using the monobath solution. The third and fourth strips represent samples of the two-bath system. Note the small differences in base fog and image density between the two strips. The third strip was processed in 0.4 sec while the fourth was processed in 0.2 sec. Table IV gives a quantitative comparison of the base fog and image densities of these film strips.

There seems to be little doubt that the developing time can be reduced even further. From the data available it would appear that a developing time of 0.1 sec is feasible. However, conclusive experiments have not been carried out since the present equipment does not permit such high-speed processing without a complete redesigning of the equipment.

TABLE IV

Film Density Relationship of Different Processing Techniques

Film No.	Processing Technique	Base Fog Density	Image Density
1	Single-step	1.66	2.4
2	Monobath	0.68	1.52
3	Two-bath, 0.4-sec dev	0.31	0.97
4	Two-bath, 0.2-sec dev	0.12	0.92

The rubber seal of the transparent fixing chamber has been a point of great concern. The seal must sustain the abrasive action of the film while it is being transported and also the chemical action of hot 50% hypo solution. The original experiments were carried out using neoprene and silicone rubber. This material gave excellent results insofar as sealing was concerned. However, the seal wore after a relatively short time of operation. At the end of 40-hr operation the rubber seal had worn down approximately $^1/_{32}$ in. Materials such as stainless steel, teflon, and nylon were tested with no success. These materials would produce a good seal at the beginning of the operation, but soon after, the film emulsion would be continuously scratched and the seal would be lost. This condition was traced to foreign particles and crystallization of the developing solution near the seal. This solid matter was transported by the film. It was concluded that the soft seal allows the foreign particles to slide away between the ring seal and the film, thus scratching only a very small section of the film. Based on this observation, experiments were carried out using other soft materials. The G. L. Martin Company, which has modified one of the Kenyon equipments, has adopted a silicone rubber containing teflon. This material has given an improved service of 28%. It is believed that greater improvement in this field is possible.

The two-bath technique has increased the amount of information obtainable from the equipment. When the single developing solution was used, the beam intensity of the PPI scope had to be kept very high in order to produce a dense image on the film. This increases the overall size of the scanning light beam to a point where there is noticeable loss of definition. However, since the two-bath system produces an increase in contrast ratio and a considerable decrease in base fog compared to the single developing solution, it has been possible to diminish the scanning spot light intensity to a very low level. This has resulted in increased definition and improved discernability of targets. It is the opinion of some PPI observers that the new presentation of the projected

PPI information is actually better than the presentation obtained by direct viewing of the PPI screen. This is probably due to the fact that the PPI presentation projected on the screen remains in full view of the observer for the full interval of one antenna sweep, but when the observer views the PPI presentation directly, he has to depend on the persistence of the phosphor screen of the PPI which produces full brilliancy for a limited time only.

The two-bath system has solved a very pressing problem in the field of PPI presentation. It is believed that high-speed development has other applications in the study of transient phenomena.

Acknowledgments

The author is indebted to Steven Levinos, Willard C. Burner, and Joseph Belmonte for their cooperation and assistance in arriving at the successful conclusion of this project.

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An Evaluation of the Crabtree-Ross Procedure for Residual Hypo in Processed Film

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A study of the Crabtree-Ross test for residual hypo in processed film was made. The validity of this test had been questioned for two reasons: (1) the hypo values obtained on flashed film areas were higher than those for lower density areas, and (2) the hypo value obtained was not always indicative of the amount of film fading upon aging.

The Crabtree-Ross hypo values obtained on freshly processed film were compared with the values obtained by two other independent test methods. The three methods of hypo estimation were compared over a range of concentrations from that found on poorly washed film (150 μg per sq in.) to films that were more completely washed (10 μg per sq in.). A close correlation was found between results obtained by the three methods, which indicated that the Crabtree-Ross method accurately measured the amount of residual hypo in freshly processed film.

Aging the film for several weeks showed that a considerable amount of trithionate was formed in the film. Prolonged aging (2–3 months) gave some evidence of tetrathionate formation. Since both these polythionates do not respond to the Crabtree-Ross test and yet will cause fading in film, the use of this test on aged film samples could cause an error approaching 100% in the estimate of the fading potential. Thus, it was concluded that the present test procedure is invalid for predicting the fading propensity of aged film samples. The silver sulfide stain test now used for testing paper and film for residual hypo appears to be a more accurate measure of the fading potential of processed film.

For the past twenty-five years, the Crabtree-Ross test has been used to estimate the residual-hypo content of processed film. At the present time, it is the basis for the American Standards Association specifications for the measurement of residual-thiosulfate content in films[1] used for archival purposes. It is a particularly attractive test method because of its simplicity and the speed with which analyses can be carried out.

Analyses for residual hypo customarily are made on a clear area of the processed film if such an area is available. It has been observed in these Laboratories[2] that, in the same film specimen, areas of high image density contain more residual hypo, as determined by the Crabtree-Ross method, than comparable clear areas do. The difference might be as much as a factor of 5, and it has not been clear whether this difference is real with respect to hypo content, or is due to some idiosyncrasy of the method. In addition, there appeared to be a rapid decrease in the hypo content of films on aging, as indicated by the Crabtree-Ross test. This decrease in apparent hypo content was not accompanied by a corresponding decrease in the fading potential of the film, and, accordingly, the usefulness of the Crabtree-Ross procedure for the examination of aged film samples is open to serious question.

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The purpose of this study was to show how accurately the Crabtree-Ross test actually measured the hypo content by comparing these results with those obtained by other independent test methods. In addition, the study was designed to explain the observations of other workers concerning the apparent higher retention of hypo by image areas as well as the decrease of hypo content as a function of aging. This paper is mainly concerned with an evaluation of the present test procedure for fresh and aged film samples and does not deal with the merits of alternate methods of hypo estimation.

Description of the Crabtree-Ross Procedure

The Crabtree-Ross test for residual hypo is based upon the turbidity formed when thiosulfate ion reacts with a solution containing mercuric chloride and potassium bromide. The test procedure for processed film consists in taking a known area of film (usually 1 sq in.) and immersing it in a solution containing 2.5% mercuric chloride and 2.5% potassium bromide. After allowing the sample to soak in this solution for 15 min, the solution is shaken thoroughly and its turbidity is compared with that produced by known concentrations of thiosulfate. This comparison can be done visually or by means of a photometer.

Effect of Salt Concentration on the Determination of Hypo Using the Crabtree-Ross Procedure

Initially it was thought that the retention of hypo by film, even during a thorough washing operation, must be an adsorption type of phenomenon. This would then account for the tendency of image areas to retain more hypo than clear areas. On image areas, there is an opportunity for hypo to adsorb onto developed silver surfaces whereas, in clear areas, this possibility is minimized. If the adsorptive forces are great enough, this could lead to low results in the test procedure now used. In the event that the hypo is strongly adsorbed in the image areas, a solution of high ionic strength should be more effective in removing the hypo present in the film layer by adsorptive displacement. A reagent containing a high salt concentration thus might be expected to give a higher result for hypo content.

In order to test this hypothesis, the effect of certain salts on the formation of the Crabtree-Ross turbidity was established by using known solutions rather than film samples. First, a study was made of the effect of potassium bromide concentration on the turbidity formed with hypo. The results of this study are graphically summarized in Fig. 1.

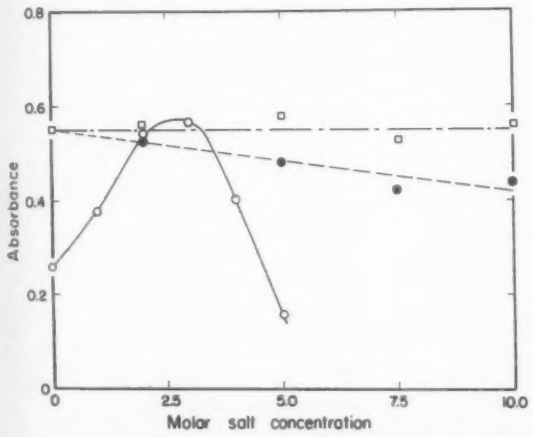

Fig. 1. Effect of salt concentration on the Crabtree-Ross test: O, KBr (+2.5% $HgCl_2$); □, KNO_3 (+Crabtree-Ross reagents); ●, K_2SO_4 (+ Crabtree-Ross reagent).

On using mercuric chloride alone, the turbidity formed with a given amount of hypo was 50% less than that formed with an equivalent amount of hypo and the Crabtree-Ross reagent. On the other hand, a large excess of potassium bromide prevented the formation of a turbidity. It is evident from Fig. 1 that the composition of the Crabtree-Ross reagent is optimum for producing maximum turbidity with a given amount of hypo. This maximum appears at a mole ratio of approximately 2 bromides per mercuric ion. The use of mercuric chloride and potassium bromide rather than just mercuric bromide, however, is necessary since the solubility of mercuric bromide is only 0.5 gram per 100 ml. It is evident then that the reagent is actually a mercuric bromide–chloride complex. As will be pointed out subsequently, this complex accounts for the selectivity of the reagent for hypo.

Figure 1 also illustrates the effect of two other salts on the turbidity formed with the Crabtree-Ross reagent. Potassium nitrate was found to have no apparent effect, whereas high concentrations of potassium sulfate retarded the formation of the turbidity to a slight extent.

On the basis of the evidence just given, 10% potassium nitrate was employed in the Crabtree-Ross reagent to see if the higher ionic strength would result in increased yield of hypo from film samples owing to adsorptive displacement. Analyses were carried out on freshly processed samples of Kodak Micro-File Film which had been washed for varying lengths of time in order to provide a range of hypo concentrations. Table I shows a comparison of the analytical results obtained by using the normal Crabtree-Ross procedure and the procedure modified by the addition of 10% potassium nitrate to the reagent.

TABLE I

Comparison of the Recovery of Hypo With and Without Excess Inert Electrolyte

Sample Wash Time (min)	Micrograms of Hypo per Square Inch	
	Crabtree-Ross Value	Crabtree-Ross + KNO_3
4 Clear	56, 72	75, 71
4 Flashed (d = 3)	73, 73	77, 85
10 Clear	22, 19	25, 25
10 Flashed (d = 3)	39, 49	36, 49

It is evident that the reagent containing potassium nitrate does not result in a significantly higher recovery of the hypo present, especially in the case of flashed film samples. This indicates that adsorption does not decrease, to any significant extent, the recovery of hypo from processed film in the usual Crabtree-Ross procedure. Levenson and Sharpe[3] have shown that small amounts of hypo are very strongly absorbed to the silver image. These workers showed that only strongly adsorbed ions such as sulfite and iodide could remove the hypo. It is our belief that the mercuric chloride–potassium bromide reagent also successfully removes the hypo. Results obtained by the benzidine procedure presented in the latter part of this paper make this point more conclusive.

Comparison of Rate of Development of Turbidity in Standards and in Actual Film Samples

According to the procedure now used for the Crabtree-Ross test, the method is calibrated against stand-

ard turbidities which are developed by adding the Crabtree-Ross reagent to aqueous solutions containing known amounts of sodium thiosulfate. Obviously, this method of standardization does not reproduce exactly the conditions under which samples are analyzed. It was thought a difference must exist between the particle size of a turbidity formed by a substance diffusing from a gelatin layer and that produced by reaction of two aqueous solutions, and this difference might lead to a systematic error in the analysis of film samples.

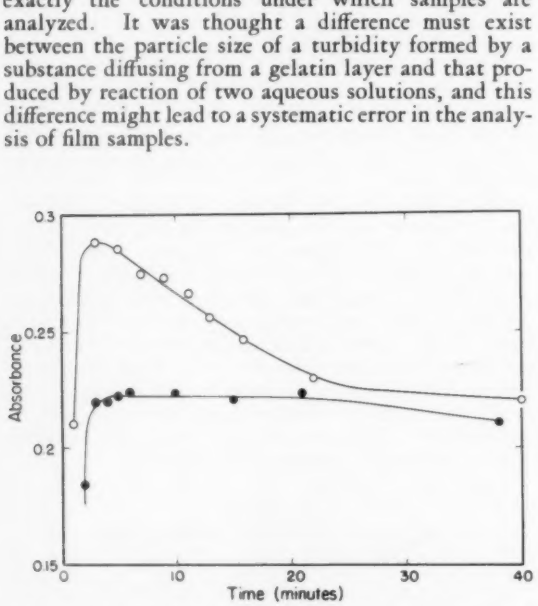

Fig. 2. Time-dependence of the Crabtree-Ross turbidity: O, film sample containing 112 μg of hypo per sq in.; ●, hypo standard (100 μg per 10 ml).

Figure 2 shows the turbidities developed in two samples of hypo, one a standard solution, the other an actual film sample. It is evident that the particle sizes of the turbidities actually differ. The turbidity which is formed in the presence of the film sample appears initially to have a smaller particle size. If the turbidities are read after 15 min, as the present ASA method suggests, the error would be no greater than 10% of the amount present. For most practical applications, this is a tolerable limit.

Accuracy of the Measurement of Residual Hypo on Freshly Processed Film

The results given in Table I do not show conclusively that image areas retain more hypo than nonimage areas during the washing of a processed film. When a well-washed, flashed film sample which contains no hypo is immersed in the Crabtree-Ross reagent, the image rapidly turns white. Qualitative tests show that this white product contains mercurous and silver halides, apparently formed according to the reaction:

$$2\,Ag + 2\,HgX_2 = 2\,AgX + Hg_2X_2,$$

where X is either chloride or bromide. Crabtree-Ross tests on flashed samples of Micro-File Film that had been thoroughly washed to remove the last traces of hypo gave no detectable turbidity. This substantiated the earlier work of Crabtree and Ross[4] indicating that the metal halides generated by the reaction with the silver image were not diffusible and therefore could not contribute to the turbidity formed in the test procedure when hypo is present.

In order to establish unequivocally whether or not the Crabtree-Ross test measured accurately all of the residual hypo present in a freshly processed film sample, a series of processed Micro-File Film samples were analyzed for hypo, using the Crabtree-Ross test and two other independent methods. The two independent methods used were the benzidine method for total sulfate and the direct iodimetric titration of hypo.

Both clear and flashed samples of Micro-File Film were processed and washed for given periods of time, dried, and then analyzed within 6 hr by the Crabtree-Ross method. The iodimetric analyses were also carried out within 6 hr after processing. Because the benzidine method is based on a determination of total sulfur, the time factor was not important and, in this case, samples were analyzed 3 days after processing.

Experimental Procedure

Reagents

Crabtree-Ross reagent was prepared by dissolving 25 grams of Reagent Grade mercuric chloride and 25 grams of Reagent Grade potassium bromide in distilled water, and diluting the mixture to 1 liter. This solution was filtered through an HA Millipore Filter before use.

A standard iodine solution was prepared by dissolving 15 mg of Reagent Grade iodine and 15 mg of potassium iodide in distilled water, and diluting the mixture to 1 liter. This solution was standardized against a known thiosulfate solution prepared by weight. A dead-stop titration method[5] was used.

The benzidine solution was prepared by dissolving 0.5 gram of benzidine hydrochloride in 100 ml of distilled water. The resulting solution was filtered through an HA Millipore Filter to remove undissolved particles. Benzidine solutions were not kept for more than one day, because of decomposition.

Crabtree-Ross Procedure

The Crabtree-Ross test was run on fresh film samples shortly after processing. Circular punch-outs of film, approximately 1 in. in diameter (0.7812 sq in.), were dropped into 10 ml of Crabtree-Ross reagent. The film sample was allowed to stand in this solution without agitation for 15 min, then shaken to distribute the turbidity uniformly, and, finally, the absorbance was read at 400 mμ in a 1-cm cell.

A calibration curve for this test was prepared by adding known amounts of hypo, with micropipets, to 10-ml portions of Crabtree-Ross reagent, allowing turbidity to develop for 15 min, agitating the solution, then reading the absorbance at 400 mμ. A visible

spectral curve of the turbidity indicated 400 mμ to be the most sensitive wavelength at which to make readings.

Benzidine Procedure

The benzidine test was run on film samples by taking circular punch-outs, approximately 0.75 in. in diameter (0.4422 sq in.), and subjecting them to the usual micro Carius digestion. The digest was then dissolved in water and any silver chloride filtered off through a sintered glass filter of medium porosity. The filtrate was evaporated to dryness and taken up in 1–2 ml of distilled water containing one drop of 0.2*M* acetic acid. One milliliter of benzidine hydrochloride solution was then added, and the samples were kept at 60 C for 15 to 30 min. The solutions were filtered through two layers of Whatman No. 40 Filter Paper in a micro Buchner-type funnel by suction and the precipitate was washed with several milliliters of a 1:1 water–ethanol solution which had been previously saturated with benzidine sulfate. The filter pads were then dropped into 5 ml of 1:10 hydrochloric acid and heated at 60 C for 10 min. The resulting solutions were cooled, diluted to 25 ml with 1:10 hydrochloric acid, and the absorbance was read at 250 mμ in a 1-cm cell. This procedure is an adaptation of one given by Anderson.[6]

Iodimetric Procedure

Samples of freshly processed film were analyzed for residual hypo by titrating the hypo with a standard iodine solution using a dead-stop titration technique. Circular samples of film, 0.75 in. in diameter (0.4422 sq in.), were taken for analysis. The samples were dropped into 15 ml of distilled water containing one drop of 1*M* sulfuric acid and stirred for 20 min with a magnetic stirrer. The solution was then titrated with 10^{-4} *M* iodine solution according to the well-known reaction:

$$2\ S_2O_3^{=} + I_2 = S_4O_6^{=} + 2I^{-}.$$

The end-point was detected using the dead-stop method and could be reproduced to ±0.05 ml of 10^{-4} *M* solution. This uncertainty amounts to ±2.5 μg of $Na_2S_2O_3 \cdot 5H_2O$ or approximately ±6 μg per sq in. of film area under the conditions of the test. On fresh film samples where there has been no opportunity for the hypo to decompose, the method is assumed to be correct within these limits of uncertainty. The results of the analyses on processed film samples using the three analytical methods are summarized in Table II.

Results

It is evident that, on freshly processed film samples, the Crabtree-Ross and the iodimetric method were in essential agreement. It follows, therefore, that the Crabtree-Ross method, when applied to fresh samples containing hypo in the range studied (from 10 μg per sq in. for completely washed samples to 150 μg per sq in. for poorly washed samples) gives entirely valid results.

TABLE II

Comparison of Crabtree-Ross Test With Iodimetric and Benzidine Methods for Hypo

Sample Wash Time (min)	Micrograms of Hypo per Square Inch	
	Crabtree-Ross Value	Iodimetric
4 Clear	75	79
4 Flashed	149	154
10 Clear	53	60
10 Flashed	127	139
20 Clear	10	12
20 Flashed	25	27
		Benzidine
4 Clear	67	218
4 Flashed	93	365
10 Clear	45	44
10 Flashed	77	70

The comparison of the Crabtree-Ross method with the benzidine method gave divergent results. On poorly washed film samples, the benzidine method gave a much larger value than the Crabtree-Ross method, presumably because the benzidine test included the sulfur from any residual sulfite or alum remaining on the film. On more completely washed samples, however, both methods gave essentially the same results. These results clearly indicate that the Crabtree-Ross test does, in fact, give an accurate estimate of the hypo content of freshly processed film, both in the clear and in the flashed areas. Furthermore, it is evident that the high results obtained on flashed film samples are actually due to a greater retention of the hypo by the film during the washing operation rather than an idiosyncrasy of the Crabtree-Ross test on these samples.

Mode of Decomposition of Residual Hypo in Aged Film

Previous studies[7] have indicated that there is a close correlation between the hypo content and the fading potential of a freshly processed film. This relationship, however, does not hold when applied to processed film samples that have been aged for a period of time. In general, aged film samples show considerably more fading than can be accounted for by the hypo value as determined by the Crabtree-Ross test. It follows, therefore, that the residual hypo in aged film must decompose to some other sulfur bodies which do not respond to the Crabtree-Ross test but cause fading in film.

In attempting to identify the various degradation products of hypo in aged film samples, the polarographic technique appeared to be particularly useful. Trithionate, tetrathionate, pentathionate, and hexathionate ions have been reported to be polarographically distinguishable.[8] The thiosulfate ion itself gives only an oxidation wave and therefore would not be expected to interfere with the identification of the polythionates mentioned.

Polarograms run on samples that had been aged for 2–3 months indicated the presence of small amounts

of another reducible material giving a reduction wave in the same region as that of the tetrathionate ion. This suggests that tetrathionate may be a further decomposition product of thiosulfate, but the evidence is not considered conclusive.

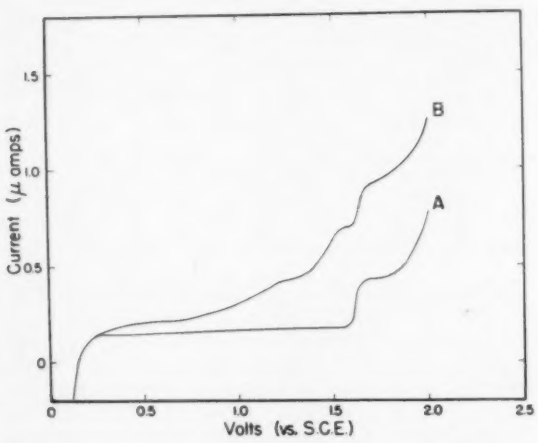

Fig. 3. Polarograms of extracts of processed flashed Kodak Micro-File Film: A, freshly processed sample; B, sample aged for 2 wk.

Figure 3 shows recorded polarograms of extracts of a freshly processed film and a sample of the same film made two weeks after processing. In polarogram A, the only reducible material present is an unidentified material extracted from the film base. Polarogram B shows a definite second reducible wave preceding the same wave found in A. This second wave was found to have a half-wave potential ($E_{1/2}$) of -1.47 v vs. a saturated-calomel reference electrode (S. C. E.). A sample of potassium trithionate gave an $E_{1/2}$ of -1.45 v in this same medium. From the magnitude of the diffusion current, it was estimated that roughly 30% of the initial thiosulfate had been converted to trithionate. The decrease in residual hypo from freshly processed film to that which has aged for several weeks is about 70% for flashed areas. Thus, it is clear that the trithionate content of aged film samples is very nearly the same as the hypo content.

Response of Various Polythionates to the Crabtree-Ross Test

Since there was some evidence of the presence of polythionates in aged film samples, it was necessary to establish the behavior of these polythionates in the Crabtree-Ross procedure as well as to determine their photographic fading behavior. To answer these questions, a series of polythionates were synthesized using reported procedures[9,10] and the response of these polythionates to the Crabtree-Ross test was measured. The thionates tested were: sodium sulfite, sodium dithionate, potassium trithionate, and sodium tetrathionate.

On using the Crabtree-Ross procedure, none of the polythionates mentioned formed a turbidity. The reagent as used appeared to be selective for hypo and did not respond to its decomposition products.

It should be noted that mercuric chloride in the absence of potassium bromide formed a turbidity with potassium trithionate and sodium tetrathionate as well as sodium thiosulfate. In comparing the sensitivity of mercuric chloride with the ordinary Crabtree-Ross reagent, it was found that the former was only half as sensitive for thiosulfate. No attempt was made in this study to determine the exact nature of the turbidities. It should be noted, however, that in neither case is the precipitate simple mercurous chloride or bromide[11] as was originally reported.[4]

Fading Behavior of Potassium Trithionate

Because polarographic studies indicated that trithionate was the major decomposition product of hypo, a sample of this material was tested for fading properties.

Well-washed Micro-File Film samples bearing an image of typed matter so wedged as to vary from quite dense to extremely light over the area of each frame were spotted with solutions of sodium thiosulfate and potassium trithionate. The concentrations of these materials per unit area were calculated from the weight of the drop and the diameter of the spot. These film strips were then incubated for 12 days at 130 F and 90% RH.

Fading was evident on both the trithionate and the thiosulfate spotted samples but was judged to be more severe in the case of thiosulfate. The data do indicate, however, that trithionates are potentially dangerous fading agents.

The fading tests, along with the fact that these higher polythionates do not give a turbidity with the Crabtree-Ross test, clearly account for the discrepancies noted earlier between fading potential and Crabtree-Ross hypo values on aged film samples. From polarographic estimates of the trithionate content of aged film samples and the fact that the trithionate ion, while causing fading, will not respond to the Crabtree-Ross test, it was decided that the Crabtree-Ross values on aged film samples could be in error by as much as 100% insofar as the fading potential is concerned.

Summary

The Crabtree-Ross test has been examined with respect to its validity for the measurement of residual hypo in processed film. It has been found that the test accurately measures the hypo present. Depending on the age of the film, however, the relationship between hypo content and fading propensity varies. On fresh samples, there is a direct relationship; hence, the Crabtree-Ross test is a good measure of the fading potential. Aged film samples, however, have been shown to contain fading agents other than hypo. Trithionate ion, whose presence has been established, does not respond to the Crabtree-Ross test and yet does cause fading. Thus the use of the Crabtree-

Ross test on aged film samples does not give a good estimate of the fading potential of that film. Further work on the adaptation of the silver nitrate stain test for determining the fading potential of aged film samples is being carried out.

Acknowledgment

The authors wish to express their appreciation to G. T. Eaton and R. W. Henn for their interest and cooperation in this study.

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The Use of Electronic Image Intensification in Cinéfluorography

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Image intensification devices may be advantageous in cinéfluorography by reducing the overall cost of equipment and by decreasing the patient's exposure to radiation. Parallel evaluations of two image intensification systems are described. The resolution of the systems studied was found to be comparable to direct cinéfluorographic techniques, but the intensification provided was not sufficient to offset the limitations except in special cases. The chief limitation of the image intensifier was the 5-in. input image size.

In 1896, one year after the discovery of x-rays by Wilhelm Conrad Roentgen, John Macintyre of Glasgow, Scotland, undertook to produce x-ray motion pictures.[1] He arranged his camera behind a lead screen which had an opening to match the gate of his camera; and by covering the gate with black paper to shut out visible light, he was able to obtain direct x-ray motion pictures of the leg motions of a frog. But, understandably, there were difficulties in simultaneously manipulating his subject, the x-ray apparatus, and the camera. Consequently, to complete cycles of motion and to match the actions of different series, he conceived the technique of animation. By this method he managed to piece out forty frames of continuous action. Three frames from his first film are shown in Fig. 1.

Macintyre first presented his x-ray motion pictures of the frog before the Glasgow Philosophical Society late in 1896. His pictures created a popular sensation, and by this early demonstration Macintyre established himself beyond question as the originator of cinéroentgenography.[2]

It is interesting to note that Macintyre's achievements were accomplished at a time when as yet only a few people in the world had ever seen motion pictures of any kind. It was, in fact, in February of the same year that the Lumiere brothers' "Cinématographe" was given its first press showing at the Empire Theatre, in London; in March that R. W. Paul demonstrated his "Theatrograph" at the Royal Institute; and in April that Thomas Edison's "Vitascope" arrived in London from New York.

Macintyre's success with his frog's leg pictures inspired other investigators to try similar techniques. It soon became evident, however, that although Macintyre had devised a way of getting substantially instantaneous exposures, the method gave adequate exposures only with very small objects like the frog's leg. Individual radiographs of larger objects like human bone required exposures of 15 min to an hour or more. In consequence, very little was accomplished with x-ray motion pictures until many years later, after the successful development of much more powerful equipment.

Early investigators of medical applications of x-radiation were not as acutely aware of the hazards of exposure to radiation as we are today. Were it not for the restrictions imposed by the dangers of excessive exposure, there is little doubt that x-ray motion-

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* Formerly the U.S. Army Signal Engineering Laboratories.

Fig. 1. The first x-ray motion picture, 1896 — three frames from Dr. Macintyre's famous film showing a frog's leg in action.

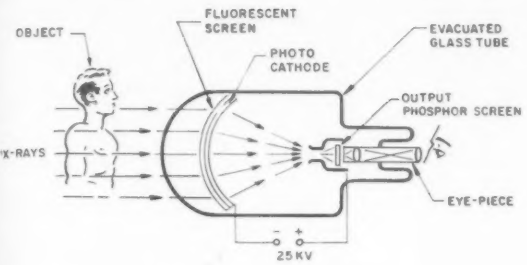

Fig. 2. Philips image intensifier.

picture techniques would be used much more extensively than is actually the case at the present time.

X-ray generators now have sufficient capacity to penetrate the thickest body sections with ease. Fluorescent screens now have sufficient conversion efficiency for x-rays without objectionable persistence. Camera lenses and film have sufficient speed without objectionable loss of detail. But, considering the system as a whole, the system response remains slow to a degree that radiation exposure becomes the limiting factor in this application. This limiting factor is so severe that some desirable diagnostic procedures must be eliminated altogether. During the past several years, improvements in the relative speed or response of fluorescent screens, camera lenses, and film have increased the over-all speed and decreased the radiation exposure by a factor of about 5. This improvement, while worthwhile, is not quite enough to bring the radiation exposure down to manageable proportions for routine procedures. Furthermore, these improvements have not helped to reduce the cost of the equipment, which is always a major stumbling block to routine operation. Some substantial increase in system response without a corresponding increase in cost is required before this technique can become a routine procedure.

The development of electronic image intensification during the past ten years was first looked upon as the necessary break-through. Indeed for some diagnostic procedures, it has provided the necessary jump in response; but, unfortunately, it does not resolve all of the problems. As is frequently the case, a gain is made in one factor with an accompanying loss in another. The required jump in system response is provided by electronic image intensification, but the maximum input aperture of the device is a 5-in. diameter* circle which is much too small to view critical objects such as the adult human heart.

The Image Intensifier

The Philips image intensifier[3] is an evacuated glass tube containing a fluorescent screen on a thin aluminum base (Fig. 2). In contact with the screen is a photoemissive surface. X-radiation after passing through an object strikes the fluorescent screen. The screen fluoresces, giving off light which impinges point by point on the photoemissive surface. Electrons are released from this surface as a result of the light exposure. The image leaving the surface is now an electron image which is accelerated through a 25-kv field and electrostatically focused onto an output phosphor, reduced approximately 10 times in size. The output phosphor is observed through a magnifying eyepiece or is coupled to a motion-picture camera for a permanent record of the subject. The amplification arises from the high energies of the electrons striking

* An image intensifier having an 11-in. diameter input aperture is now manufactured by Philips.

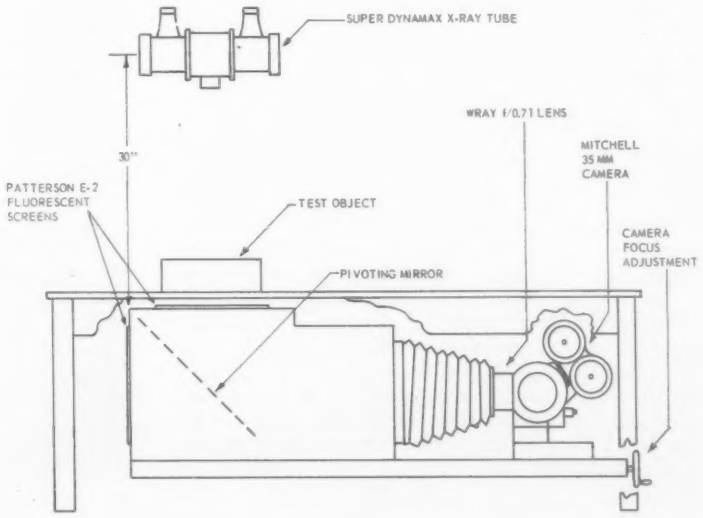

Fig. 3. Functional diagram of conventional cinéfluorographic system.

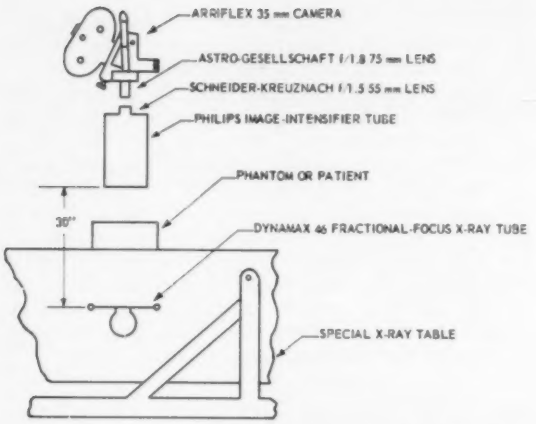

Fig. 4. Functional diagram of the Philips image-intensifier tube system.

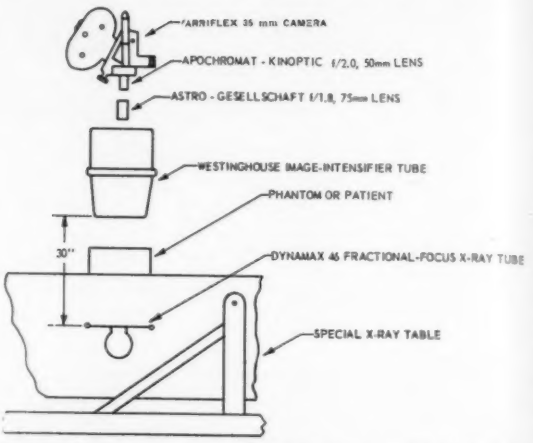

Fig. 5. Functional diagram of the Westinghouse image-intensifier tube system.

the output phosphor and from the electrooptical minification of the image size. The Westinghouse tube is roughly similar in design but uses a minification factor of 5 rather than 10.

Initially, the high voltage on the tube imparts extra energy to the photoelectrons, thus making the fluorescence of the viewing screen or output phosphor brighter than that originally produced on the photoemissive surface. This is known as the lumen intensification of the tube. Finally, by virtue of the N-times electrooptical reduction, the light proceeds from an area smaller than that of the photoemissive surface, so that here an extra gain of N^2 is obtained. The total intensification is the product of the lumen intensification and the gain from the reduction of the image size. Unfortunately, most of this total intensification is lost in the optical coupling system to the camera. Apparently, for this application, only the intensification resulting from the electric field contributes to the gain in sensitivity.

The Apparatus

The equipment used in this study consisted of three complete cinéfluorographic systems. The first was a reference system incorporating maximum response components typical of existing cinéfluorographic systems. The second and third systems were identical except for the type of image intensifier and lens coupling to the camera. The lens combinations were chosen to provide a final image of nearly the same size for the two electronic systems, which would best utilize the 35mm film frame. The final image size for the two systems was approximately 19.2 mm. The system used for reference is shown in Fig. 3. The system using the Philips tube is shown in Fig. 4, and the system using the Westinghouse tube is shown in Fig. 5. A view of the special x-ray table with the Westinghouse tube mounted in position is shown in Fig. 6.

Experimental Procedure

The conventional system was operated through a series of exposures to determine the factors of milliamperes, time, and kilovolts required to produce a film density of 1.0 through simulated body tissue. Following this, the two systems utilizing image intensifiers were operated through a similar series of exposures. The distance between the x-ray source and the sensing element or input fluorescent surface was the same for each system and was representative of what would be used in practice. The family of curves, usually referred to as "technique" curves, for the conventional and the electronic systems are shown in Fig. 7.

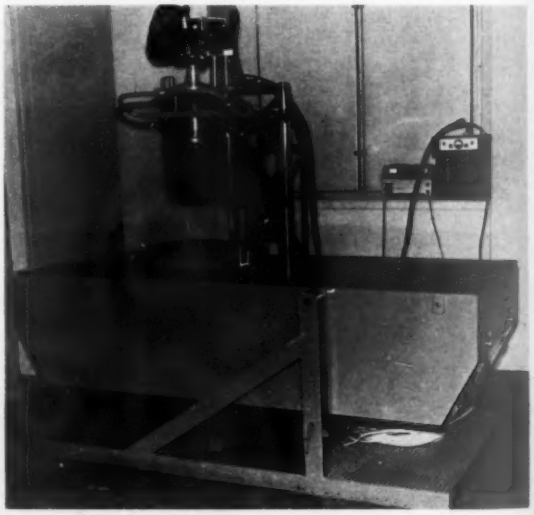

Fig. 6. Special x-ray table in a horizontal position.

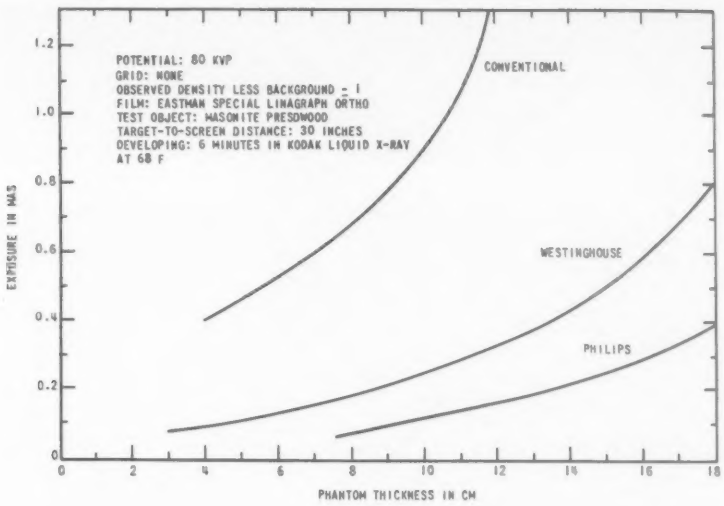

Fig. 7. Constant-density curves for the conventional, the Philips image-intensifier, and the Westinghouse image-intensifier cinéfluorographic systems.

The systems containing the image intensifiers were then compared to the conventional system with reference to the reduction in exposure required to produce a unit film density. The amplification factor for each image intensifier was defined as the inverse of the reduction of exposure to produce a unit density — all other factors being held constant or normalized to constant values. Since the conversion efficiency of fluorescent materials is dependent on the incident photon energy and since the input phosphor of each of three systems was somewhat different in composition, the amplification factor was not constant with respect to the incident photon energy. While the actual spectra of two x-ray tubes used would not be exactly the same, it was assumed that they would be sufficiently similar so as to permit comparison of amplification factors as a function of the peak voltage applied. This comparison is shown in Fig. 8.

The ability of these systems to resolve images was measured by the use of a simulated tissue and blood-vessel object. Absolute resolution of high-contrast objects such as black lines on a white background have no meaning in the examination of clinical objects. Therefore, conventional resolution measurements do not adequately describe a relative figure of merit for an x-ray system. To determine the resolution of an x-ray system intended for clinical use, it is necessary to use a test object which approximates the contrast changes in the human body.

Among the types of human tissue most difficult to

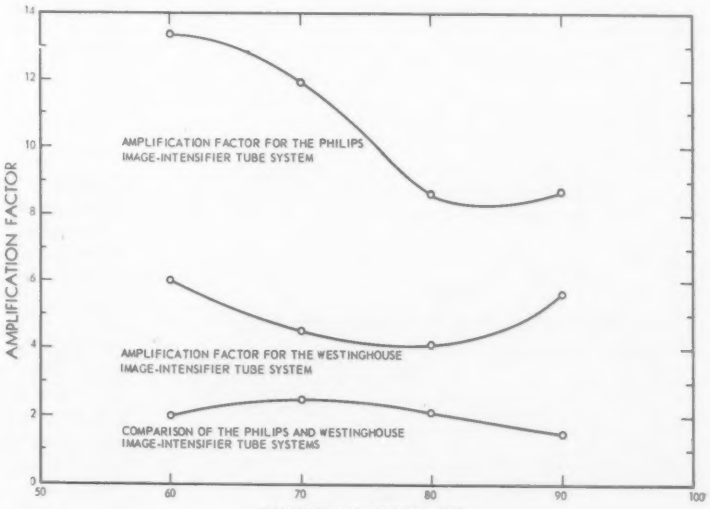
AMPLIFICATION FACTOR FOR THE PHILIPS IMAGE-INTENSIFIER TUBE SYSTEM
AMPLIFICATION FACTOR FOR THE WESTINGHOUSE IMAGE-INTENSIFIER TUBE SYSTEM
COMPARISON OF THE PHILIPS AND WESTINGHOUSE IMAGE-INTENSIFIER TUBE SYSTEMS
AMPLIFICATION FACTOR
X-RAY ENERGY IN KILOVOLTS - PEAK

Fig. 8. Comparison of cinéfluorographic systems.

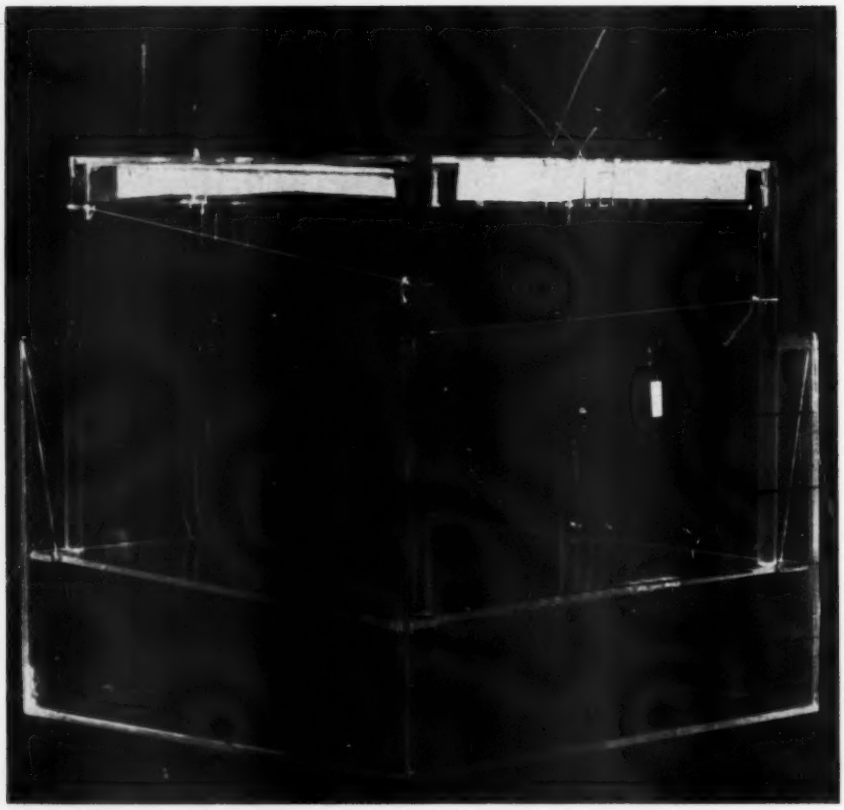

Fig. 9. Special test object used to simulate veins in the body.

visualize by fluoroscopic techniques are the blood vessels. Blood vessels can be visualized only when the absorption of x-radiation by the vessel becomes substantially different from the absorption by surrounding tissue. This change in absorption is usually accomplished by filling the vessels with a radiation opaque material that will not interfere with the normal function of the vessel. A typical contrast media for blood-vessel visualization, called Diodrast, contains a high percentage by weight of iodine.

A test object to simulate the vessels was constructed of small bore polyethylene tubing, suspended in water, and filled with different concentrations of Diodrast. The test object is shown in Fig. 9. In the experiment the test object was placed in the x-ray beam and the image recorded on the film as in normal procedure with a human subject. The film was then inspected to determine the minimum detected tubing bore for each concentation of Diodrast and for each system. The results of these measurements for 35% Diodrast are listed in Table I.

TABLE I

Comparison of Resolutions of Fluorographic Systems

System	Minimum Resolvable Tube Diameter (mm)
Conventional Ciné	1.67
Philips Image Amplifier and Ciné Camera	0.58
Westinghouse Image Amplifier and Ciné Camera	0.76

Conclusions

The results of this experimental program were that the image intensifier tubes provide a significant increase in over-all system sensitivity. The cost of either tube is not excessive and, in fact, may be offset by a reduction in cost of the x-ray apparatus compared to the conventional system. The resolution of the tubes tested was at least as good as in the conventional system.

A negative factor, and a major one for this application, is the limited field of view of the image intensifier. The input fluorescent surface in both the Philips and the Westinghouse tubes is a circle of 5-in. diameter. The object being examined is closer to the x-ray source than is the input phosphor and its image is magnified. Therefore, the maximum object size is more nearly a circle 3.5–4.0 in. in diameter. This

severely restricts the application of image intensifiers in diagnostic procedures. It would appear then that while the image intensifier offers an improvement in sensitivity in the examination of small objects, it is by no means the answer to the radiation problem in cinéfluorography.

Acknowledgments

The authors wish to acknowledge the contributions to this paper of H. Stephen Weens, M.D.,Emory University School of Medicine, and Arthur Williamson and Harry Youmans, Engineering Experiment Station, Georgia Institute of Technology. The experimental program was carried out by the Georgia Institute of Technology under contract with the U.S. Army Signal Engineering Laboratories. The Emory University School of Medicine participated in the program by providing medical consultation, space, and equipment.

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Neutral Image Tones with Kodak High Resolution Plates

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The very high resolution and sharpness of Kodak High Resolution Plates (similar to Kodak Spectroscopic Plates and Films, Type 548), combined with their practically total lack of granularity, make them especially suitable for test objects used in the study of image structure. With the usual processing in Kodak Developer D-19, however, images of moderate density usually exhibit a pronounced green cast, which may restrict the usefulness of the test object. The addition of various substances to the developer has therefore been investigated in an attempt to find an additive for controlling image tone.

A suitable substance was found in sodium thiosulfate (hypo). By trial it was found that Kodak Developer D-8,[1] to each liter of which about 20 grams of hypo were added, produced suitable image tones, free from stain, for development times of the order of $1^1/_2$ min at 68 F. The remainder of the processing was done as recommended for these plates.

Since Kodak Fixing Bath F-24[1] was at hand ready-mixed, we added our hypo in this form in the proportion of 80 cc to each liter of developer. This amount of F-24 represents 19.2 grams of hypo plus some sodium sulfite and bisulfite, which have the effect of changing the pH and the sulfite concentration of the solution by an unimportant amount.

The addition of hypo to the developer in the required proportion results in a speed increase of from one-half to one stop, with either no change in gamma or a slight increase. The sharpness does not seem to be impaired nor the graininess perceptibly increased. The Callier *Q*-factor is approximately constant at 1.14 over the density range from 0.1 to 0.9. This *Q*-factor is slightly greater than that for the Kodak Wratten Neutral Density Filter No. 96.

The effect on image tone is shown by the spectrophotometric curves in Fig. 1, which are for a development-time series on Kodak High Resolution Plates developed in the mixture described in this note. The development times are marked on the curves. These curves are on a density basis, and it can be seen that it is possible to shift the image tone from greenish through approximate neutrality to blue by increasing the development time. The exact combination of hypo concentration and development time varies with individual coatings of the emulsion, but by a proper adjustment, it is possible to produce tones which are visually quite neutral for all densities. The spectrophotometric curves of such samples having densities below about 1.5 are reasonably flat; for denser samples, the curves rise slightly at the red end.

Image tone is often claimed to be a function of grain size, and Koerber[2] and Pinoir, Thornton, and Baby[3] have established such a relationship in certain cases. In the present instance, however, a relationship has not been found. For example, in Fig. 2, A is an electron micrograph of grains from a sample developed in straight D-8, which is definitely greenish, and B is a similar micrograph from a sample developed in the mixture of D-8 and F-24 for $1^1/_2$ min at 68 F, which is neutral. There is no perceptible difference in grain size. A possible reason for this lack of correlation between grain size and color has been given by Cassiers,[4] who found that the addition of mercaptan

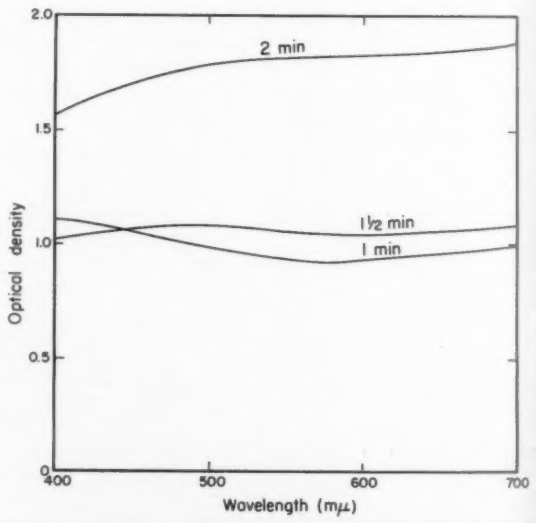

Fig. 1. Spectral transmission (on density scale) of images on Kodak High Resolution Plates developed in Kodak Developer D-8 plus 80 cc of Kodak Fixing Bath F-24 per liter of developer. The development times are indicated on the curves. Exposure times for the samples were adjusted to give roughly similar densities.

* Communication No. 1959 from the Kodak Research Laboratories. Received 25 April 1958.

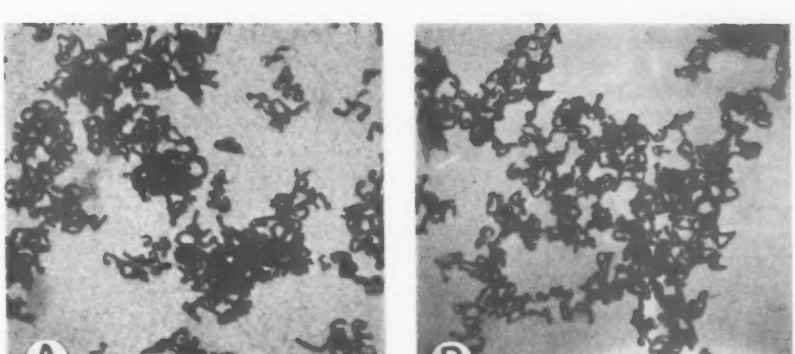

Fig. 2. Electron micrographs (30,000 ×) of images on Kodak High Resolution Plates, developed for 1½ min at 68 F. A, developed in D-8 alone; B, developed in D-8 plus F-24, as described in text.

compounds to a special type of emulsion caused a shift from yellowish to blue-black tones. He concluded that, in this case, the tone shift was related to changes in the surface character of the grains. James and Vanselow[6] have found that, for tone shifts produced by changes in the pH or the nature of the developer (instead of by addenda), the color of the deposits likewise appears to be determined by the characteristics of the silver-grain surfaces rather than by the size of the developed grains.

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A Revision of the Relation Between American Standard Exposure Index and DIN Speed Resulting From a Recent Revision of the German DIN 4512 Standard

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An empirical relationship is derived relating $\log_{10}$ (American Standard Exposure Index) and DIN speed. The DIN speeds used in the relation are those computed according to the specifications for speed evaluation as given in the recently revised German Standard DIN 4512 Blatt 1, November 1957. A table is given listing corresponding values of American Standard Exposure Index and DIN speed.

In a paper entitled "A Comparison of DIN Speed and American Standard Exposure Index for Black-and-White Negative Roll and Sheet Films,"[1] a linear relationship between $\log_{10}$ (American Standard Exposure Index) and DIN speed was established as a simple means of predicting one value from the other. The empirical relation resulted from a determination of the DIN speed and fractional-gradient speed of each of 54 black-and-white roll and sheet films. The exposing and processing of the 54 films were performed according to the German[2] and American[3] standards of speed specification which were in effect at the time of publication.

A new revision of the German standard, released in November 1957,[4] results in a new definition of DIN speed.

In the earlier DIN 4512 standard,[2] the DIN speed was defined as

$$\text{DIN} = \log_{10} \frac{0.36}{E_{0.1}},$$

where $E_{0.1}$ is the exposure in meter-candle-seconds required to produce a density of 0.1 above fog.

In the revised DIN standard, the DIN speed is defined as

$$\text{DIN}^* = \log_{10} \frac{0.49}{E_{0.1}}.$$

Hence,

$$\text{DIN}^* - \text{DIN} = \log \frac{0.49}{E_{0.1}} - \log \frac{0.36}{E_{0.1}}$$

$$\text{DIN}^* - \text{DIN} = \log \frac{0.49}{0.36} = 0.134 = 1.34/10°.$$

This means that, for a given $E_{0.1}$, the new DIN* rating is 1.34/10° higher than the old DIN rating.

If the films used in the author's investigation[1] are rated by the new DIN 4512 standard instead of the old DIN 4512 standard, the relation between DIN* and $\log_{10}$ (exposure index) will be

$$\log_{10} (\text{exposure index}) = -0.175 + 1.064\ \text{DIN}^*, \quad (1)$$

or, the inverse,

$$\text{DIN}^* = 0.164 + 0.939 \log_{10} (\text{exposure index}). \quad (2)$$

The new German standard states that an exposure index of 100 is equivalent to a DIN speed of 21/10°. Implied in this statement is the assumption that a given increment of log (exposure index) corresponds to an equal increment of DIN* speed over a wide range of film speeds. Hence, the relation between log (exposure index) and DIN* which is implied is

$$\log_{10} (\text{exposure index}) = -0.100 + 1.000\ \text{DIN}^*. \quad (3)$$

The fact that the coefficient of DIN* in Eq. (1) is different from unity is due to the experimental finding that the difference in log exposure between the ASA and DIN* speed points is not constant throughout the entire range of film speeds as it is assumed to be in the German standard.

Figure 1 is a plot of the relations given in Eqs. (1) and (3). The solid line is the empirical Eq. (1), and

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* The asterisk will be used in this paper to indicate DIN speed computed according to the November 1957 revision of the DIN 4512 standard.

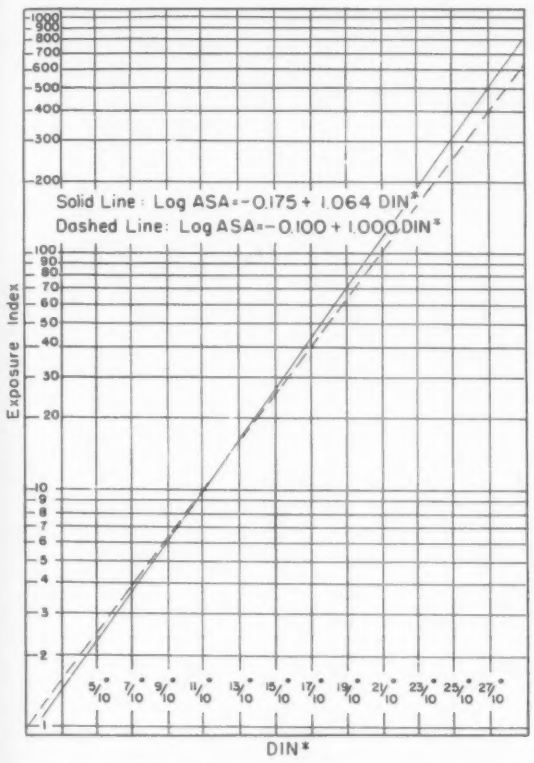

Fig. 1. The solid line is the empirically derived relation given by Eq. (1). The dotted line is the approximation Eq. (3), as implied in the DIN 4512 Blatt 1 standard.

the dotted line is the approximation Eq. (3), as implied in the DIN 4512 Blatt 1 standard.

Table I offers a means of conversion among the following speed measures:

(a) Arithmetic Exposure Index;
(b) Logarithmic Exposure Index ($LEI = 5 - 10 \log_{10} E_{0.3\bar{G}}$);
(c) Values of DIN* speed computed from Eq. (2), using the values of exposure index from (a); and
(d) Values of DIN* speed computed from the less accurate approximation Eq. (3), using the values of exposure index from (a).

In Column (e) of Table I are the differences between the values of DIN* speed specified by Eq. (2) and the values of DIN* speed specified by the approximation Eq. (3).

TABLE I

Table of Conversion Among Various Measures of Speed

(a) American Standard Exposure Index	(b) Logarithmic Exposure Index	(c) DIN* Speed from Eq. (2)	(d) DIN* Speed from Eq. (3)	(e) Column (c) minus Column (d)
1000	41°	29.8/10°	31/10°	−1.2/10°
800	40	28.9/10	30/10	−1.1/10
650	39	28.0/10	29/10	−1.0/10
500	38	27.0/10	28/10	−1.0/10
400	37	26.1/10	27/10	− .9/10
320	36	25.2/10	26/10	− .8/10
250	35	24.2/10	25/10	− .8/10
200	34	23.2/10	24/10	− .8/10
160	33	22.3/10	23/10	− .7/10
125	32	21.3/10	22/10	− .7/10
100	31	20.4/10	21/10	− .6/10
80	30	19.5/10	20/10	− .5/10
64	29	18.6/10	19/10	− .4/10
50	28	17.6/10	18/10	− .4/10
40	27	16.7/10	17/10	− .3/10
32	26	15.8/10	16/10	− .2/10
25	25	14.8/10	15/10	− .2/10
20	24	13.8/10	14/10	− .2/10
16	23	12.9/10	13/10	− .1/10
12	22	11.9/10	12/10	− .1/10
10	21	11.0/10	11/10	0/10
8	20	10.1/10	10/10	.1/10
6	19	9.0/10	9/10	0/10
5	18	8.2/10	8/10	.2/10
4	17	7.3/10	7/10	.3/10
3	16	6.4/10	6/10	.4/10
2.5	15	5.4/10	5/10	.4/10
2.0	14	4.5/10	4/10	.5/10
1.6	13	3.6/10	3/10	.6/10
1.2	12	2.6/10	2/10	.6/10
1.0	11	1.6/10	1/10	.6/10

It must be pointed out that the speed relationships derived in this paper are based on measurements of ASA and DIN speeds made in strict accordance with the specifications set forth in the American and German standards. The relations given in Table I may have no direct connection with the relations between the various types of film rating numbers which are used in exposure meter calculators. The latter relations must be determined by practical comparison measurements with exposure meters marked with the various types of scales.

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An Analytical Recording Densitometer

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A completely automatic recording densitometer, based on the indirect method of measuring respective integral color densities and converting them to analytical densities by computation, is described. The equipment delivers complete measurements from a 21-step sensitometric strip in 100 sec, with a performance accuracy of better than 0.01 unit of density.

In the practice of analytical color densitometry, two principal methods[1] of measurement are available: (a) the direct, or image synthesis, measurement of analytical densities, based on the principle that the absorption by dyes in the film sample can be matched by combined absorption of three wedges, each of which contains varying known amounts of one of the three dyes of the process in question; and (b) the indirect method of measuring the respective integral color densities and converting them to analytical densities by computation. Experience has shown that the latter method of coordinate transformation from integral densities provides a superior basic approach to color densitometry. The instrument to be described has been designed to evaluate equivalent neutral density, a form of analytical density. Equivalent neutral density of a component of a subtractive color process has been defined[2] as the luminous density it would have if it were converted to gray by superimposing the just-required amount of other component dyes of the process. This unit of measurement indicates the individual amounts of each of the three dye deposits.

In the ordinary types of standard neutral density instruments, white light is incident upon the film sample and the ratio of the transmitted light (P_t) to the incident light (P_o) is determined by a photometric process. The logarithm of the reciprocal of this ratio (transmittance T) is the definition of density ($D_T = \log_{10} 1/T$), which is usually expressed directly against dial or scale on the instrument. If the sample is a color film consisting of three separate dye layers on a film base, the measurement of density will give a value representing the total absorption of the white light by the three layers. This total density is integral density and it does not indicate the respective parts played by each layer in the absorptive process which are desired in the determination of analytical densities. The indirect method of determining analytical densities, which is the basis of operation of the densitometer to be described, measures spectral densities as the first step in its program. These densities are as defined but confine the light used in the measurement to narrow spectral bands, each of which corresponds approximately with the region near the maximum absorption of each component layer of the film. The three values of integral spectral densities, D_B, D_G, and D_R, are converted[1] by the use of transformation equations into equivalent neutral densities of the cyan, magenta, and yellow dyes.

General Description

For research programs and control functions pertaining to color films, the design specifications of this Analytical Recording Densitometer require that a high degree of basic accuracy, repeatability, freedom from drift, and high operational speed be necessary characteristics and that it present the integral color densities, visual densities, and analytical color densities on plotted graphs and/or punched cards, with the option of a selection of filter sets and transformation equations to match a variety of products.

An Analytical Recording Densitometer which satisfies these specifications, complete with all necessary equipment, is shown in Figs. 1 and 2. The first six of the following sections of the instrument are serially numbered in the figures according to their respective positions in the operation cycle:

1. A servo-controlled densitometer unit with a logarithmic iris modulator[3] providing a density range of 4.0, capable of balancing successively on each step of a standard 21-step sensitometric strip. Each step is read sequentially through three filters, and the information is transmitted electrically to

2. A servo-controlled, analog-buffer storage unit which stores the three respective integral densities per step for acceptance by

3. An analog computer[4] which converts the integral densities to analytical densities by any preselected transformation equation and presents the analytical density values to

4. (a) A servo-controlled recording section which converts the respective outputs to analog displacements of a recording arm which plots a series of

Communication No. 1973 from the Kodak Research Laboratories, presented at the Annual Conference, Asbury Park, N.J., September 1957. Received 18 July 1958.

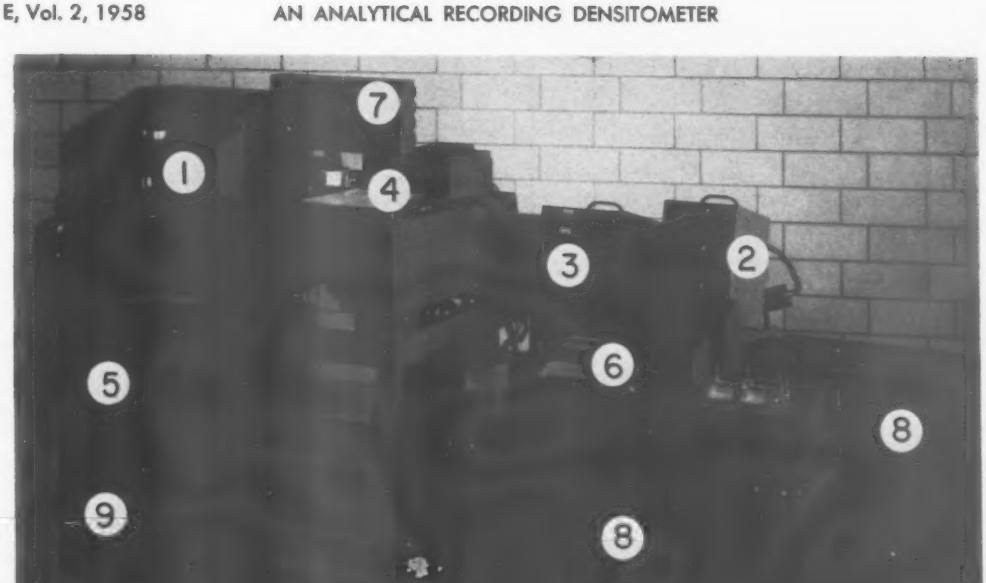

Fig. 1. General view of densitometer.

respectively different colored dots on graph paper, and (b) an analog-to-digital converter, which provides discrete 3-digit numbers (analytical density values) to

5. A digital-buffer storage unit, which feeds
6. A standard summary card punch.

These three sections are control and accessory units:

7. A control and selector panel.
8. Cabinets for housing three servoamplifiers, power supplies, etc.
9. Programming relays, interlocking relays.

Cycle of Operation

The typical cycle in the measurement by this apparatus of the characteristics of a standard 21-step sensitometric strip of a color photographic film follows. Details of each of the units performing in this cycle will be discussed later.

A single main switch controls the entire apparatus. After this is turned on, the proper zeroizing adjustments are made, the appropriate set of filters is selected, a coordinate transformation matrix is selected to match the film, and the other sensitometric characteristics of the strip, such as log E increment, number of steps, etc., are set on the control panel (7, Fig. 1). The strip is inserted and the "start" button is pushed to begin operation.

The densitometer, with the blue filter required to provide one of the previously mentioned narrow bands of spectral light in place, automatically starts to balance on the integral density D_B of Step No. 1. The output of the densitometer, a voltage across a precision potentiometer geared to the light-modulator, is fed to the blue section of a servo-controlled, analog-buffer storage unit (2, Fig. 2). The blue-section servo follows the modulator movement of the densitometer until a balance is obtained. Both units are then stopped; the blue filters are automatically replaced by the green ones; and the densitometer is ready for the measurement of the green

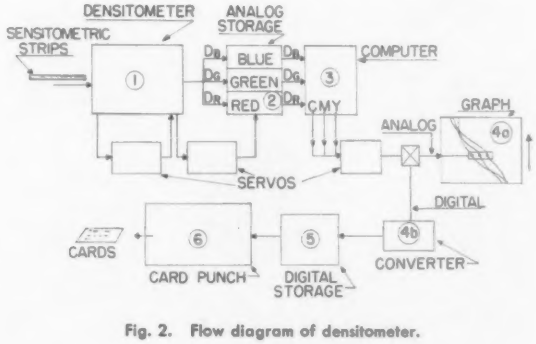

Fig. 2. Flow diagram of densitometer.

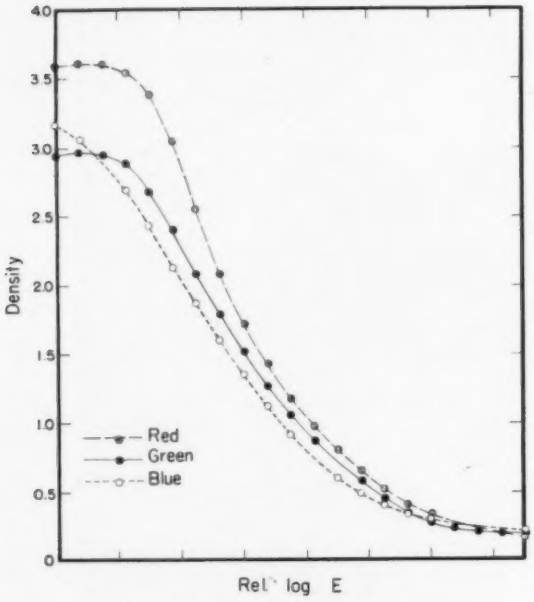

Fig. 3. Sensitometric strip and plotted points.

integral density of Step No. 1. The blue storage unit is ready to supply the computer (3, Fig. 2) with the blue value, and the green storage unit is switched into action to receive the green measurement from the densitometer. This cycle is repeated until the green and the red measurements are completed.

After the red section of the storage unit has come to balance, the servomotor which drives the recording-pen arm (4a, Fig. 2) is connected to the cyan equivalent neutral density output of the computer. The recorder arm comes to balance and the cyan pen makes a colored dot on the *D*-log *E* graph paper. An analog-to-digital converter (4c, Fig. 2), which is geared to the arm, enters the cyan density value in the digital-buffer storage section (5, Fig. 2) as a 3-digit number, and the card punch perforates the card in the appropriate columns, as described later. This cycle is repeated for the magenta and the yellow measurements, respectively. The graph paper table is now advanced by the selected log *E* increment and the entire sequence is set into motion for Step No. 2, which has been moved to the reading position. All three servo-units may be running simultaneously, and the blue density of a step may be read before the final recording of the previous step is completed. Figure 3 shows a completed graph, with the three curves drawn manually through the plotted points

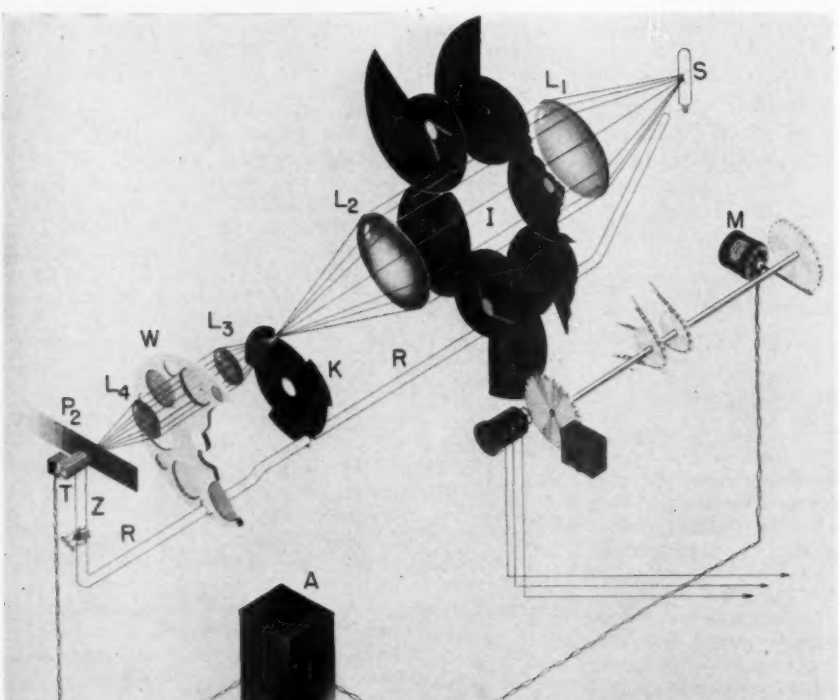

Fig. 4. Schematic, perspective view of densitometer.

made from the sensitometric strip placed above it. The drawing of the curves is not required for normal operation.

Three standard punch cards are required for each strip of twenty-one steps in addition to a master card which accompanies the sensitometric strip. Cards of various colors are used to designate department, type of density, etc. The first sixteen columns of the master card contain the coded data pertaining to the strip, such as emulsion code, coating numbers, and roll numbers. These data are duplicated on each of the three cards as each card appears in the cycle. The seventeenth column of each card receives a serial number 1, 2, or 3, and the remaining sixty-three columns of each card receive the 3-digit density numbers for seven of the twenty-one steps to provide total information for one sample strip on the three cards.

The Analytical Recording Densitometer

A semipictorial, perspective view of the densitometer section is shown in Fig. 4. Light from a 6-v, 108-w, coiled-filament lamp S is collimated by the lens L_1, passes through the aperture of a logarithmic iris diaphragm I, focused by the lens L_2 at the chopping disk K, relayed by the lenses L_3 and L_4 to the sample plane P_2, and transmitted through the sample to the multiplier phototube T. A second, or reference, beam of light is carried by Lucite plastic rods R from the lamp to the phototube. The iris modulator provides a 10,000:1 attenuation of the main beam by a direct drive which is linear with respect to log transmission of the iris aperture. The two beams reaching the phototube are alternately chopped at 60 cycles/sec by the disk K and filtered by a series of pairs of filters in the wheel W. The large filters in the main beam are narrrow-band interference filters and the small ones in the reference beam are Kodak Wratten filters of respectively corresponding peak transmission.

A zeroizing unit is placed in the reference beam at Z (Fig. 4). Figure 5 shows a schematic view of this unit and its relation to the filter wheel. The green reference filter is shown in position while the green interference filter is in the main beam, and the Lucite rod is shown to be transmitting the green reference light to the phototube. The enlarged view of the unit at the lower right shows the round aperture to be divided into three equal sectors, each of which is covered with a Wratten filter to match its corresponding interference filter on the wheel. Each is also covered by an opaque vane which is successively adjusted in or out of the sector as each of the filter pairs is brought into play. Because each zeroizing filter is essentially opaque to the transmissions of the other two reference filters, each one is not affected by the other two vane adjustments.

Differences in illumination from the alternating light beams on the multiplier phototube result in a pulsating d-c output at the anode. The a-c component of this is filtered and amplified by a servoamplifier A (Fig. 4) and is used to drive the servomotor M on the modulator until the effects of the light beams are equal and the signal in the preamplifier is zero. This null system makes the balance point independent of phototube sensitivity, amplifier gain, or fluctuations in the light source.

Figure 6 is a photograph of the system oriented to correspond with Fig. 4: X is the exit side of the modulator; K is the chopping disk driven by a synchronous motor, and automatic phasing is accomplished by the small a-c generator mounted above the motor, overloading the motor when the chopper is out of phase until it slips the disk into the correct angular position; motor C, through a Geneva movement, drives the filter wheel to the successive positions; D is the sample-receiving chute and illuminating box for indexing the filmstrip; E is the output potentiometer linked to the modulator; M is the servomotor which drives the modulator to balance; housing G contains the multiplier phototube and the preamplifier; the sample carriage is driven by the wire loop H; Z is the set of three zeroizing knobs of the system shown in Fig. 5.

The 35mm sensitometric strip is inserted in the chute D until a centrally marked step is framed in an illuminated aperture to place Step No. 1 on the optical axis. The strip is turned 90° along guides which place the first step orthogonally on the optical axis. This bend in the film maintains the plane of the measured area uniformly flat. The guide slots which hold the film are automatically moved as the film progresses from step to step to prevent sliding contact of the film with the nosepiece of the pickup system. When the measuring cycle is started, a clamp automatically grips the film. This clamp is attached to a wire loop which is driven intermittently and quietly by a pitman action and pulls the strip through its series of positions. At the end of the cycle, the strip is pushed back to its starting position ready to be removed by the operator. A selector knob on the control panel provides for a choice of the number of 0.05 log E increments of the graph table per step of the sample in order to

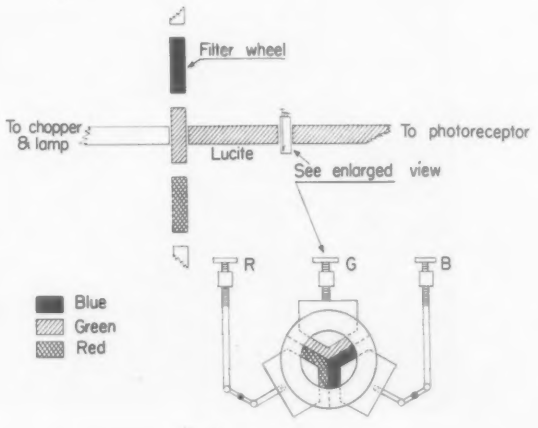

Fig. 5. Zeroizing unit.

compensate for the various types of sensitometric exposure on the strips. Short or long strips may be used.

The filter mechanism automatically shows which group of filters is in use by lighting a printed window on the control panel. A button resets the instrument to starting conditions at any time during a run. Three switches in conjunction with dials on the densitometer, computer input, and recording section permit the operator to check the calibration of the densitometer against a check strip, or the accuracy of the computer section against any desired inputs and the accuracy of the servotransfers and analog-to-digital conversions.

Each of the three identical, separate units for storing the values of D_B, D_G, and D_R in the computer input and storage section is a plug-in chassis and is interchangeable. For checking the computer, a forward and reverse drive control is provided with a manual fine adjustment to enter any given density into the unit. The computer section holds the separately plugged, interchangeable drawers, each representing a set of constants of the conversion equations. A switch gives a choice of five separate sets of constants for the transformation equations for various color films. One of the sets of constants yields an output identical with the input. The individual drawers are easily accessible for adjustment or removal.

TABLE I
Accuracy of Each Section of the Densitometer

	Accuracy	
	Mean Deviation	Sigma
Light-modulator	−0.0015	0.0048
Follower servos:		
Blue	.0000	.0018
Green	.0020	.0030
Red	.0009	.0023
Computer:		
To Yellow E.N.D.*	− .0022	.0036
To Magenta E.N.D.	− .0001	.0034
To Cyan E.N.D.	.0018	.0028
Modulator values to E.N.D.		
Yellow	− .0034	.0042
Magenta	.0032	.0062
Cyan	.0027	.0037
Punch and Digital Converter	.00135	.0031

* Equivalent neutral density.

Performance

The accuracy of the Analytical Recording Densitometer was analyzed by H. C. Schmitt Jr., of these Laboratories, by comparing ASA standard densities and the values of equivalent neutral densities computed from the integral spectral densities with the respective values obtained from the instrument for

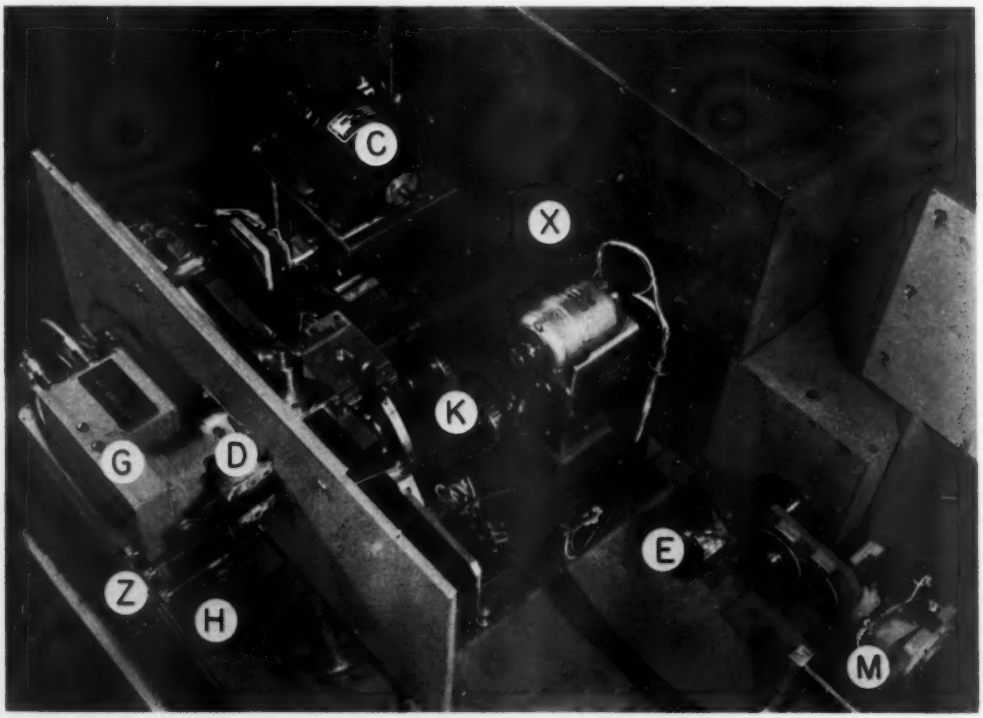

Fig. 6. Modulator, chopping disk, filter wheel, and sample holder.

forty-two samples of one type of Kodachrome Film. Performance figures were obtained for the light-modulator, the follower servos which set the modulator values into the analog computer, the computer, and the recording section (including the IBM Punch). Performance is described by the mean deviation, or systematic bias, between the two sets of values and also by the standard error of estimate (sigma), giving limits about the biased mean inside of which two-thirds of all readings can be expected to fall. The performance figures, given in density units in Table I, opposite, show that, in no case, was the expected error of any section as great as 0.01 density, and in only one case did it exceed 0.005.

This is only one determination of the accuracy of the instrument with one set of equations. Some day-to-day variation exists in each of the sections, and another determination would show somewhat different individual errors, although substantially the same over-all results. The mean deviations in the follower servos and punch sections could be reduced at the expense of using components of improved linearity. On the basis of these results, however, the accuracies of the individual sections of the instrument and of the instrument as a whole are well within the tolerances necessary for normal operations.

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Moisture in Photographic Film and Its Measurement

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Photographic film will absorb water in either the liquid or gaseous phases. This characteristic is of importance to the physical and photographic properties of film. With some review, the hygroscopicity of photographic film and its effect on some of the physical and photographic properties of film are discussed. Essential to the study of the effects of moisture on photographic film properties is the measurement of moisture itself in film. A description of a number of analytical methods, chemical, physical, and electrical, for measuring the moisture content of photographic film is included. Some of these methods, discussed briefly, are included for historical interest only. A more detailed description is given of two methods, one of which is based on an evacuation procedure, and the other on an electrical hygrometer technique.

From the early days of the manufacture of photographic film on flexible, transparent base, the moisture content of the film has affected to some degree the quality of the film, both physically and photographically. Photographic deterioration, static markings, curl, and brittleness were recognized as problems in those days as well they are at present. Because of the realization that these and other characteristics were related to the moisture content of the film, the necessity for manufacturing photographic products under controlled atmospheric conditions was recognized.

As films became photographically more sensitive and as physical requirements for use in mechanical equipment became more demanding, small variations in moisture content became more important and, in addition to close control of the manufacturing conditions, accurate measurement of moisture content became a necessity. Such measurement was a requisite for (1) investigational work relating photographic and physical characteristics of film products to moisture content, (2) selection of suitable packaging materials to maintain moisture content constant until use by the customer, and (3) quality control in manufacturing operations.

The relationship between film characteristics and moisture content has been discussed previously.[1, 2, 3, 4] This relationship will be covered somewhat generally in this paper as a review and also as an introduction to the discussion of the moisture analysis methods.

The Moisture Equilibrium Curve for Photographic Film

Photographic film absorbs water in either the liquid or gaseous phases, this absorption being different in the various component layers. Absorption in the liquid form, of course, is important in the processing operations, but absorption of water vapor from the surrounding air or from other hygroscopic materials is also of importance in the behavior of the film. The interchange of moisture between air and film is rather complex and will not be discussed here. It is sufficient to say that the moisture content of film is almost completely a function of the relative humidity of the atmosphere and not the absolute humidity. Thus, at 50 F and 60% RH, for example, film holds more moisture than it does at 80 F and 40% RH, even though the absolute humidity of the former is less (32 grains/lb of dry air) than of the latter (62 grains). It is true, however, that the moisture content of cellulosic materials is not entirely independent of dry bulb temperature, and it is known that for a given constant relative humidity photographic films hold slightly more moisture the lower the temperature. This dry bulb temperature effect, however, may be considered negligible in its effect on the properties of film.

The relationship between moisture content and relative humidity of the atmosphere is shown in Fig. 1, which is a moisture equilibrium curve for a typical sheet film. Such a curve is determined by permitting film samples to remain for a sufficiently long time at a series of controlled relative humidities to achieve equilibration of moisture content between the samples and the atmosphere. After such equilibration, the samples are analyzed for their moisture content, and the resultant relationship between moisture content and relative humidity is given in the curve. Both the level and shape of the moisture equilibrium curve provide useful information and permit ready conversion between values of per cent moisture and equilibrium relative humidity.

Strictly speaking, the term relative humidity is used to indicate the amount of water vapor in air relative to the maximum amount it could contain at that temperature. Inasmuch as film moisture

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content is a function of relative humidity, it follows that photographic and physical characteristics of a film may be said to vary with either the moisture content or the equivalent relative humidity. However, it is convenient and usually desirable to convert moisture content of film and similar materials into terms of equilibrium relative humidity, because such conversion offers a common basis of expression for measurements made on materials having different moisture capacities. For instance, it is preferable to say that two films are brittle at 15% RH rather than that they are brittle at moisture contents of 2% and 2.5% respectively, where the moisture capacities at 15% RH differ in that order.

Differences in the Hygroscopicity of the Component Layers of Photographic Film

Photographic film is not a homogeneous material. In its simplest form it is usually an emulsion consisting of silver halide in a gelatin carrier coated on a transparent, flexible base, most commonly of a cellulose ester type. This simple structure may be varied by changing the composition of the emulsion or of the base, or by coating another layer of gelatin on the side of the support opposite the emulsion for curl control or to contain antihalation dyes. Such variations in film composition produce changes in the shape and position of the moisture equilibrium curve. The greatest differences in moisture capacity of the components making up a photographic film are between the gelatin and the support, with gelatin being very hygroscopic and the support relatively nonhygroscopic.

Figure 2 shows a representative moisture equilibrium curve for a film which approximates the relatively simple film described above. Also, in the same figure, there are shown curves for the support alone and for the emulsion alone. The curve for the support is low and relatively flat; that for the emulsion is high and relatively steep; while that for the entire film approaches the curve for the support only. This position of the film curve with relation to the curves for the component parts may be explained by the fact that the slightly hygroscopic support constitutes most of the mass of the total film, while the highly hygroscopic emulsion constitutes only a small fraction of the mass. Thus, calculations of moisture content made on the weight of the whole film tend to mask hygroscopicity of the emulsion layer, and make the curve for the entire film approach that of the support. This sometimes makes it difficult to explain behavior, which may be attributed to small changes in the moisture content of the emulsion layer which are obscured in the measurement of the whole film.

Conditioning Rates

The equilibration of film to a given relative humidity is not instantaneous. The rate of equilibration of the film to the ambient condition of the

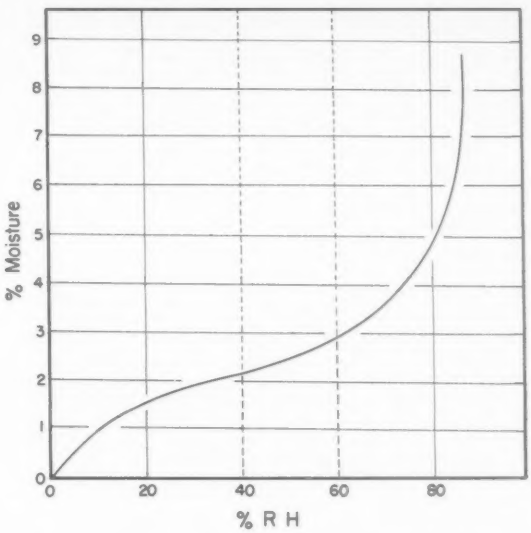

Fig. 1. Moisture equilibrium curve for a typical sheet film.

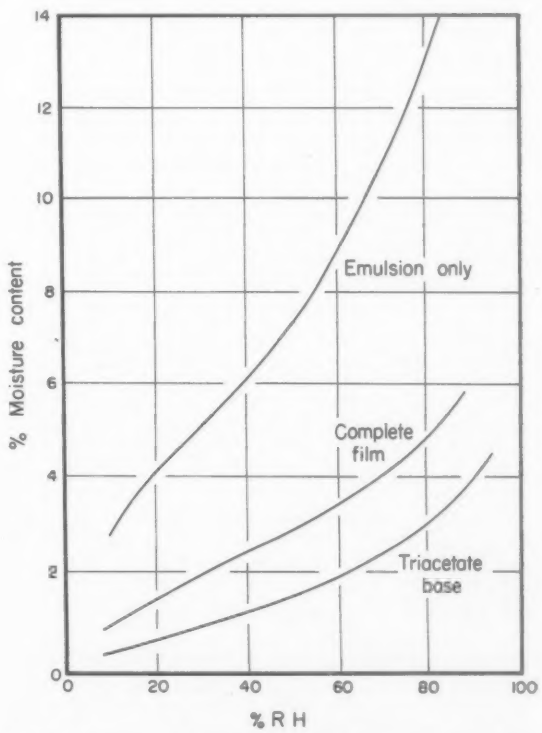

Fig. 2. Moisture equilibrium curves for total film and for emulsion and support layers separately.

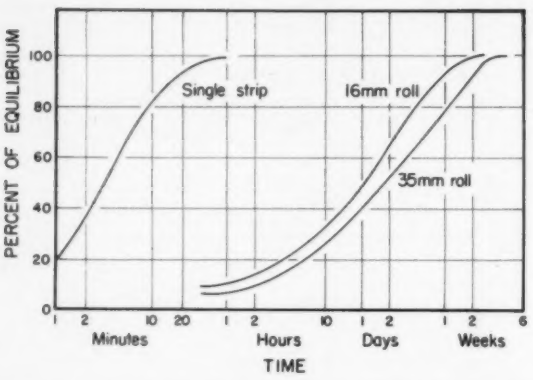

Fig. 3. Conditioning curves of a typical motion-picture positive film from 20% to 50% RH at 70 F (rolls wound at 24-oz tension, air velocity approximately 1 ft/sec).

atmosphere depends upon several factors, such as (1) physical shape of the film sample, i.e., whether wound in a roll or piled in a stack or whether individual layers or sheets are fully exposed, (2) protective layers, (3) air circulation, (4) direction of approach to the ambient condition from the wet or dry side, and (5) temperature of the air.

Figure 3 shows conditioning curves for photographic films which vary due to the degree of exposure to the atmosphere during the conditioning period.

Photographic and Physical Characteristics of Photographic Film Affected by Moisture Content

Most photographic and physical properties of film are affected by variations in moisture content as determined by the relative humidity with which the film is brought to equilibrium. Further inspection of Fig. 1 discloses that there are two points of inflection on the moisture equilibrium curve. These points are not clearly defined, but it is safe to say that below 20% RH and above 70% RH the curves are relatively steep and small changes in relative humidity result in large changes in moisture content. In the range between 20% and 70% RH the curves are almost straight and the change in moisture content for a given change in relative humidity is less. The range 40% to 60% RH, which is well within the straight line portion of the curve, is considered optimum for operation and use of Kodak films, but a given point within that range is not necessarily optimum for all film products.

In general, when films come to equilibrium outside the optimum range, undesirable changes in physical characteristics take place. In the low relative humidity range the gelatin becomes hard and tough, the support rigid, and the whole film shorter in dimension. In the high relative humidity range the film becomes soft and plastic and longer in dimension. The moisture content of the emulsion, as well as the variations in physical properties of the gelatin due to the variations in moisture content just mentioned, also has effect on the photographic properties of film. A comprehensive discussion of the properties of gelatin is given in Mees's *Theory of the Photographic Process.*[4]

In the low relative humidity range some of the film characteristics which require consideration are shrinkage, curl, and brittleness, while at high relative humidities friction, mottle, and ferrotyping effects become matters of concern. The last two are the result of the soft emulsion surface taking the impression of paper or some other surface with which it is in contact. These emulsion surface effects may often be seen in the processed as well as in the raw film.

Static markings are the photographic images of electrical discharges between film and some other material, or between the two surfaces of a film when unrolled. These markings occur in varying degrees throughout the entire relative humidity range, with the occurrence being the least in the middle range. At the low relative humidity level, a charge is produced on the film when it is moved in contact with some other material, such as interleaving paper, rollers in manufacturing equipment, or the gate of a camera. When the charge becomes great enough, a discharge takes place and the film is marked by the light produced by the discharge. In the high relative humidity range it is the separation of the layers of the moist film in the unwinding operation, either in manufacturing or in use, which causes electrification resulting in static markings.

Strain marks may be seen as sensitized or desensitized markings. These marks, which may be produced by elongation or pressure, also vary with the equilibrium relative humidity of the film. In the low relative humidity range elongation strain effects in the silver halide grains are usually greater than at higher relative humidity. In the case of strain brought about by pressure, the humidity effect is less marked, but some emulsion types are less susceptible to pressure markings at lower relative humidity levels than they are at higher levels.

Photographic deterioration on aging is also a function of the equilibrium relative humidity of the film. The data in the following tables show the change which occurs in speed, gamma, and fog as the equilibrium relative humidity of the film varies from 40% to 70% RH. These results were obtained from the testing of a typical medical x-ray film and a typical portrait film. The aging used in this work was accelerated short time–high temperature keeping (1 week at 120 F), and the changes in characteristics are not necessarily of the same magnitude as those which might occur during long time–normal temperature keeping.

In the case of the x-ray film most of the change observed is in fog growth, with the change becoming greatest in the higher relative humidity range. With the portrait type film the fog level is only slightly affected by increasing relative humidity of keeping, while most of the change occurs in the speed or sensitivity of the film.

It should be emphasized that the above discussion

Effect of Moisture Content on Keeping of a Medical X-Ray Film

Relative Humidity	Speed	Gamma	Fog
40%	180	2.70	0.06
50%	180	2.75	0.06
60%	150	2.30	0.26
70%	—	—	1.83

Effect of Moisture Content on Keeping of a Portrait Film

Relative Humidity	Speed	Gamma	Fog
40%	205	0.77	0.06
50%	190	0.73	0.07
60%	165	0.75	0.09
70%	100	0.84	0.17

of the photographic and physical characteristics of film and their relation to relative humidity is general, and that products may vary widely in their individual susceptibility to moisture effects.

Measurement of Moisture Content of Photographic Film

A well known and widely used method of determining moisture in paper is that given in both TAPPI[5] and ASTM[6] Standards. This method is very simple, consisting of weighing, drying, and reweighing the sample to be analyzed, with the loss in weight taken as the original water content. In the early attempts at determining the moisture content of film, this method was employed without success because of the loss of volatile materials other than water vapor from the film during the oven drying.

Measurement of surface electrical conductivity or of its reciprocal, resistivity, was also one of the early methods tried, and is in use to this day as a measurement of moisture studies and control. In this method the film is held in a pair of electrodes connected with an electrical bridge which is then brought into balance; the film sample constitutes an unknown resistance which can be measured when brought into balance with the other known resistances which constitute the bridge. Electrical resistivity can be plotted as a function of relative humidity, and thus values of resistivity can be interpolated for any given product for which the curve is established and be converted to terms of equilibrium relative humidity. This method can be used successfully for measuring equilibrium relative humidity of film providing all other ingredients of the film remain constant in composition and quantity, while only the moisture content varies.

Following these two methods, four chemical analysis methods have been tried. The first two, suggested by S. A. Durban of the Eastman Kodak Company Manufacturing Experiments Division, were a magnesium nitride and a xylene distillation method. The magnesium nitride analysis consisted essentially of the measurement by titration of the ammonia formed by the reaction of the water in the dissolved film and magnesium nitride. The xylene distillation method consisted of distilling from the xylene-immersed film samples, a distillate of water and xylene. The water was separated from the xylene by absorption by dry potassium carbonate in the receiving flask, and the xylene was removed by decantation and evaporation. The moisture was calculated from the weight gain of the carbonate.

The two other methods were suggested by G. L. Wernimont, then of the Kodak Park Industrial Laboratory and now of the Color Technology Division. They were the acetyl chloride and Karl Fischer methods. In the former method, the acetyl chloride reacts with the water in the dissolved film samples to form acetic acid, the quantity of the latter being determined by titration as a measure of the original water content. By the Karl Fischer Method the reagent, consisting of sulfur dioxide, methanol, and iodine dissolved in pyridine, is used in titration with the organic solvent containing water, the volume of this reagent required being used as a measure of the water content.

In general, the shortcomings of these chemical analysis methods are principally in the difficulty in getting the film into solution, the precipitation of cellulose ester from the film base in some of the methods which obscured the end point of the titration, the complexity of the techniques required, and the inability of such methods to handle the large number of analyses necessary in a short time. These methods or variations thereof are discussed more completely by Mitchell and Smith.[7]

In 1938 a weight-evacuation method of determining moisture content in photographic film was evaluated in the Manufacturing Experiments Division of Kodak Park. This method was essentially the same as the oven drying method described previously, except that the water vapor was removed by evacuation at room temperature rather than by heat. Other volatile materials, such as solvents, removed by the evacuation were so small in quantity as to be considered negligible.

The evacuation equipment shown in Fig. 4 consists of a glass desiccator connected to a Hyvac vacuum pump by means of sealed glass tubes. Into this system are incorporated a trap for catching the distillate, a calcium chloride drying tube for readmitting dry air to equalize the pressure in the system when the vacuum is broken, and a Pirani gauge for indicating the pressure. After the original weighing, the tared weighing bottles containing the samples are placed in the desiccator with the covers of the weighing bottles removed. The system is then closed, the temperature of the trap is reduced by surrounding it with a Dry Ice–acetone bath, and the pressure in the system is reduced to the range 50 -100 μ by means of the vacuum pump. The evacuation is continued for 17 hr at normal room temperature

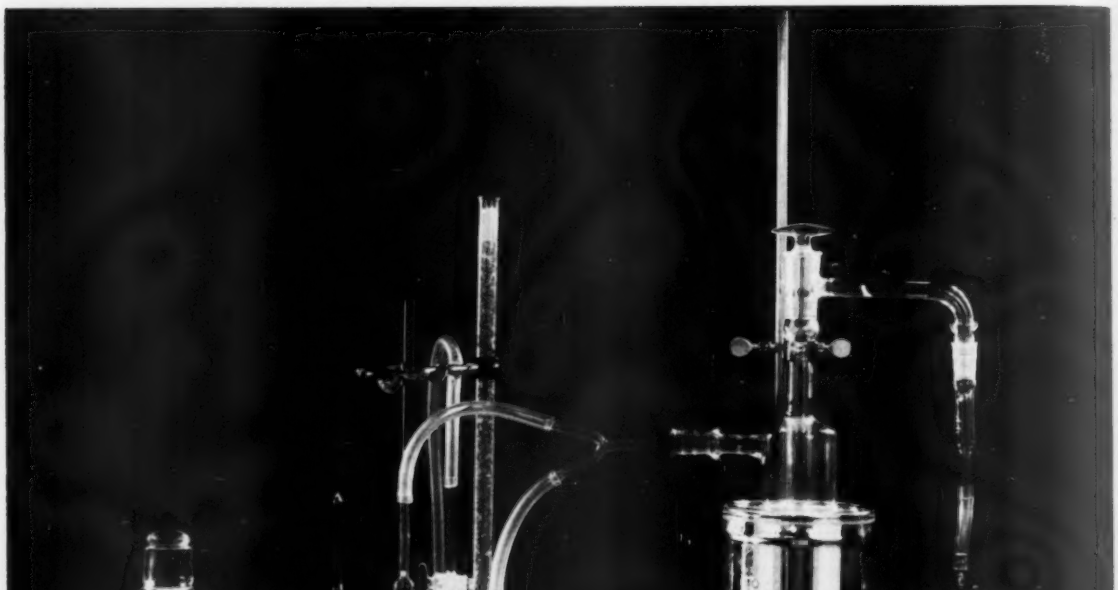

Fig. 4. Laboratory scale setup of equipment used for moisture analysis by the evacuation method.

Fig. 5. Apparatus used for moisture analysis by the electrical hygrometer method.

(approximately 80 F), after which the vacuum is broken, the sample bottles covered and re-weighed. The resulting change in weight is calculated as per cent H_2O.

$$\% \text{ Moisture} = \frac{W_1 - W_2}{W_1} \times 100,$$

where W_1 = original weight of the specimen and
W_2 = weight of the specimen after drying by evacuation.

This method requires the use of a moisture equilibrium curve to convert the per cent moisture into terms of equilibrium relative humidity. Obtaining such a curve by conditioning film samples to a series of relative humidities was described previously in this paper, and the method for analyzing such conditioned samples for moisture is the same weight-evacuation method just described.

The advantages of the weight-evacuation method are in its large capacity and ease of operation, in that only weighing techniques are required. The main disadvantages to the method are the relatively long times required for evacuation and for conditioning the samples to obtain the moisture equilibrium curve.

The most recent method to be developed and one equally as reliable as the weight-evacuation method is the electrical hygrometer method. This method, which was developed under the direction of J. T. Parker in the Manufacturing Experiments Division of Kodak Park, consists of measuring electrically the relative humidity of the air with which the film is in equilibrium in the sample bottle.

Such a method of measurement is made possible because of the particular properties of the humidity sensing element, the Aminco-Dunmore Electrical Hygrometer, manufactured by the American Instrument Company. The element consists of a hollow cylinder of polystyrene on which two fine palladium wires are wound closely together. The cylinder is dipped into a solution containing lithium chloride as a hygroscopic electrolyte, and polyvinyl alcohol which serves as a mechanical support and acts to prevent crystallization of the salt. The effectiveness of this element in measuring relative humidity accurately is possible because of the ability of the hygroscopic lithium chloride to change its electrical resistance instantly with very small changes in moisture content of the air. By use of an a-c resistance bridge and a vacuum tube voltmeter to indicate when the bridge is balanced, a resistance value corresponding to the relative humidity is obtained. Interpolation of this value in a predetermined calibration curve of resistance vs. relative humidity gives the relative humidity of the unknown sample. Figure 5 shows the electrical hygrometer apparatus and Fig. 6 shows a typical calibration curve for a sensing element.

Certain precautions must be taken and techniques used to obtain satisfactory results in using this equipment. The calibration of the elements is very important and must be done rather frequently under controlled conditions of relative humidity and temperature where the former is maintained at ± 0.5% RH and the latter at ± 0.5 F. This frequent calibration is necessary because the elements drift in their resistivity characteristics. This drift is brought about by ordinary usage in measurement, but can be exaggerated because of contamination effects by some materials, such as formaldehyde, which will cause large changes, sometimes making the element not usable for further measurement.

Sampling, of course, is important, but no more so than in the other methods described. Samples for both the weight-evacuation method and the electrical hygrometer method are the same. Four approximately 2 × 10-in. samples are placed in glass weighing bottles and wound concentrically in such a way that they line the inner surface of the weighing bottles. Sampling must be done very quickly to prevent changes in moisture which would affect the validity of the results. In measurement, the four samples are placed over the same element in sequence and allowed to remain for 10 min in each case before the reading is taken. The 10-min period is required

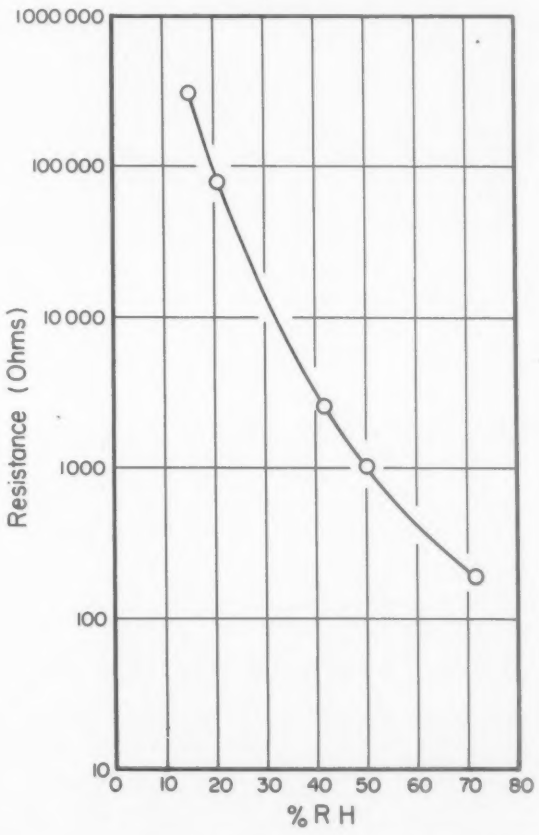

Fig. 6. Calibration curve for a sensing element of the electrical hygrometer apparatus.

to permit equilibration to occur between the element and the air in the sample bottle. The first two samples are used for preconditioning of the element to the unknown moisture level, and the last two measurements are averaged as the values for the samples.

The obvious advantages of the electrical hygrometer method are (1) speed of measurement, and (2) readings obtained directly in terms of relative humidity, eliminating the need for a moisture equilibrium curve. Some disadvantages which still remain and prevent the system from being considered ideal for all moisture measurement purposes are the necessity for calibration and measurement under carefully controlled temperatures and relative humidities. Also, this method cannot be used for analyzing liquid wet film samples, since the water affects the sensing elements.

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6. American Society for Testing Materials Method D-644-44, *Moisture in Paper, Paperboard, and Paperboard and Fiberboard Containers*.
7. Mitchell, J., and Smith, D. M., *Aquametry*, Interscience Publishers, New York, 1948, Chap. 1, p. 3.

• Book Reviews

Microphotography

G. W. W. Stevens. John Wiley & Sons, Inc., 440 Fourth Ave., New York, N.Y., 1957. 16 + 326 pp., illus., $8.50.

Microphotography is a book about photography at extreme resolution, that is, photography in which the photographs are reduced to a microscopic scale as distinguished from *photomicrography* which is photography of minute objects made with a camera and microscope.

The literature on microphotography has been somewhat limited and scattered among original papers published in many different journals, making it inconvenient for the average worker to get a broad picture of the subject. Furthermore, such information as has been available generally is not sufficiently detailed to be adequate for most purposes.

Stevens has collected those parts of the published information which seemed most important for the practice and application of microphotography. This has been supplemented by observations (many of them not published) from his own work in this field. Stevens covers the field from the period of J. B. Dancer of Manchester, England, who in 1839, within a few months of the announcement of the Daguerreotype process, tried to use it to record minute images.

Stevens' book covers the field in considerable detail, beginning with the study and introduction of microphotographic technique, through sensitive materials, processing, lenses, workroom, camera and optical bench, illumination, and microphotographic technique on to graticules (reticles), document microphotography, and microphotography as a research tool.

A more complete idea of the detail and range encompassed by *Microphotography* may be gained from the 13 chapter titles: 1. The Study of Microphotography; 2. Introduction to Microphotographic Technique; 3. The Sensitive Material; 4. The Processing of Microphotographs; 5. The Objective; 6. Establishment and Maintenance of Focus; 7. The Workroom, Camera and Optical Bench; 8. The Original and Its Illumination; 9. Microphotographic Technique; 10. Anomalous Image Formation; 11. Graticules (Reticles); 12. Document Microphotography; and 13. Microphotography as a Research Tool.

Three appendixes covering processing formulas, lens calculations, and series of exposure times, together with a name and author index and a subject index complete the volume.

Microphotography is a masterful work and well describes the principles underlying sound microphotographic practice. It is eminently suitable for serious workers in this field, be they scientists, engineers, or technicians. The book is amply illustrated with pertinent material and well written in understandable language. Technically accurate and authoritative, *Microphotography* should form a welcome addition to the literature. — *Frank Smith.*

Concepts of Classical Optics

John Strong. W. H. Freeman & Co., San Francisco, Calif., 1958. 713 pp., 414 illus., $9.50.

Every once in a while the review of a book is an interesting and refreshing assignment; this is one of those cases.

Concepts of Classical Optics is an unusually well planned textbook, moderately advanced in level, and quite thorough in scope. It is also very well written; there is an aliveness to the author's words which when combined with such other elements as the aptness of the carefully chosen quotations imparts a nice palatability to the "classical" aspects.

The early chapters deal with the wave aspects of light and electromagnetic radiation, interaction of light and matter, velocities and scattering of light. Polarized light, double refraction, interference, diffraction, coherent sources, and applications of physical optics are the subjects of other chapters. A final group of chapters covers the formation of images by single surfaces and systems of surfaces, image defects, and magnification, aperture and field.

Seventeen appendices by outstanding and competent contributors occupy more than one-third of the volume, covering many phases of interferometry, radiation detection, lens design, ray tracing, fiber optics, optical filters, diffraction gratings, wave theory of microscopic image formation, and microwave experiments.

The value of the book is markedly enhanced by the Roger Hayward illustrations which somehow draw the reader close to the subject and manage to invite him in. The clarity, accuracy, and semiformality of these pen-and-ink drawings, already known to those familiar with Strong's *Procedures in Experimental Physics*, should help to break down the resistance displayed by some students to a subject they view as complex and difficult.

There is much information in this volume, both current and classical. It will do well on your bookshelves if it finds itself in the company of other texts on optics; it probably is not the book for you if it finds itself alone. — *E. K. Kaprelian.*

• Technicalia Photographica

FRANK SMITH

• Cameras, Components, and Accessories

ETC Scope Recording Camera

An instrumentation camera, precision built, designed for long trouble-free performance, and capable of making either single-frame or moving-film recordings on 35mm film or paper, has been announced by Electronic Tube Corp., 1200 E. Mermaid Lane, Philadelphia 18, Pa. Called the ETC SM-100 Scope Recording Camera, it consists of three basic units; the camera, with its supply and take-up magazines; a sturdy universal-type mounting tripod; and a continuously variable motor-speed control which requires no warm-up.

The camera is equipped with a Wollensak $f/1.5$ 50mm coated lens, mounted in a shutter providing speeds of 1/100 to 1.0 sec. The shutter has been modified to provide electrical contact so that film will not advance unless shutter is open. The diaphragm opens $f/1.5$ to $f/8$. The object to image ratio is 4.5:1. Provision has been made for illumination of a data card.

A miniature glow lamp supplies timing marks on the edge of the film. Operator viewing is accomplished through the use of a binocular viewer which allows continuous viewing in subdued light during the recording process. The unit is designed for 115-v operation at 50 to 60 cycles. Film speed ranges from $^1/_2$ in. to 12,000 in./min in three overlapping continuous ranges.

Chadwick-Helmuth Camera-Sync Model 351

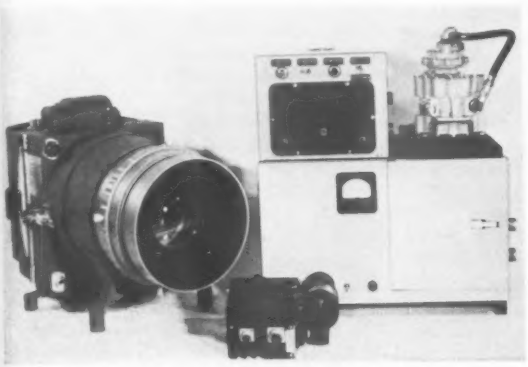
Chadwick-Helmuth Co., Monrovia, Calif., has announced development of a synchronizing device for operating a pulse-type motion-picture camera to produce slow-motion pictures of cyclic, steady-state phenomena. Called Camera-Sync Model 351, the master control for the system is the Chadwick-Helmuth Slip-Sync, which produces an electrical pulse at a repetition rate approximately 1 cycle/sec different from the phenomenon to be observed. A strobe light flashed at this new rate yields a visual slow-motion effect of 1 cycle (or revolution)/sec. The Camera-Sync then operates the camera in synchronism with the strobe lights, the strobes making the exposure.

In operation, circuitry in the Slip-Sync is used to divide the output pulse rate of the system to accommodate the mechanical limitations of the camera in use, usually about 10 frames/sec. This means that one exposure is made every number of cycles, but the phase relation of the exposures is controlled by the Slip-Sync in such a way that no information is lost. The system operates over a frequency range of 5 to 10,000 cycles/sec.

The primary application of this equipment to date is the slow-motion photography of vibration tests, but it is applicable to any cyclic phenomenon (such as rotation) from which an electrical signal can be derived.

Gordon Enterprises Recording Camera, Type 57 GE

Recently developed by and currently available from Gordon Enterprises, North Hollywood, Calif., is the Type 57 GE Recording Camera. The camera and system, designed primarily for laboratory installations, are said to be of particular value in photographing large groups of panel-mounted instruments and in wind-tunnel applications, principally because of the large (9 × 9-in.) film format size.

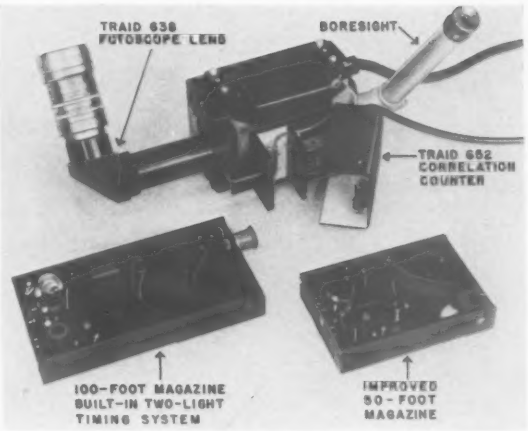


Designed to take a series of single exposures, it can be operated remotely, and through the use of an intervalometer, can be operated automatically at preselected intervals. The shutter is a between-the-lens type with a time-exposure range of from 0.2 to 60 sec and instantaneous exposures at 1/25, 1/50, and 1/100 sec. The camera cycling rate of 3 sec governs the minimum allowable time between exposures. A 12-in. *f*/2.5 Aero Ektar lens in a focusing mount provides sharp focusing at distances from 10 to 15 ft. The magazines supplied with the camera are easily changed and have a capacity of 200 ft of $9^1/_2$-in. film, which provides 250 exposures.

Traid N-9 Gun Camera Accessories

A new line of camera accessories, designed to extend the versatility, performance, and economy of the N-9 Gun Camera, has been developed by Traid Corp., Encino, Calif.

A new 50-ft magazine permits daylight threading operations and eliminates the need for metal cassettes to protect unexposed film. The film roll is simply placed in the magazine in a darkroom, after which a flange and door lock protect the film against light. A 100-ft magazine gives added capacity which greatly increases the usefulness of the N-9. The magazine is further improved by a two-light timing system which provides light traces on each side of the film. A correlation device, called the Fotocounter, forms the image of a five-digit counter on the edge of each frame of film. A periscope lens assembly, called the Fotoperiscope, permits "around-the-corner" photography for all types of 16mm cameras, including the N-9. The attachment was developed to improve photographic coverage of cameras mounted in cramped missile and aircraft installations. Fotoperiscope rotates a full 360 deg and is locked in place by a knurled ring. Built-in crosshairs can be adjusted and locked in a similar manner, thus permitting easy alignment with a particular reference line or object in the field of view. Either "C" mounting threads or the GSAP-type mounting with bolts can be provided on either end, so that the system may be used with nearly all combinations of 16mm cameras and lenses.



Use of these new accessories will save time in film loading and unloading, camera mounting, changeovers, and evaluation and correlation of test results.

Panox Super Wide Angle Camera

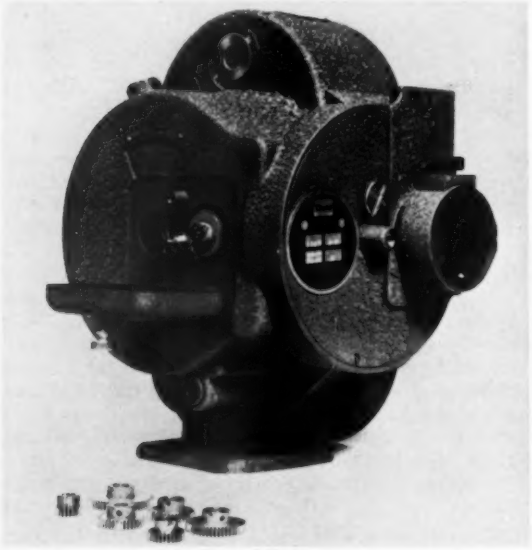
A new super-wide-angle camera, called the Panox, which covers a picture angle of 140 deg horizontally and 60 deg vertically, has been announced by Kalimar, Inc., 1909 S. Kingsway Blvd., St. Louis 10, Mo.

The camera uses 120 roll film and renders 6 exposures,

50mm by 112mm, per roll. It is equipped with a 3-element 50mm $f/2.8$ lens which can be stopped down to $f/22$. Shutter speeds are 1/2, 1/50, and 1/200 sec. There is a wire-frame and peep-sight wide-angle viewfinder and an automatic exposure counter. Each Panox camera comes with a test strip of film made with that camera.

Traid 75 Fototracker Camera

A newly designed version of the Bell and Howell Eyemo Camera, developed for use in the missile field, has been announced by Traid Corp., Encino, Calif.



The new camera, the 75 Fototracker, is built to rugged instrumentation standards and includes such special features as a variable shutter and frame speeds as high as 80 frames/sec. The 75 Fototracker is designed specifically for aircraft and missile applications requiring either high-frame rates, short-exposure times, or a combination of the two factors. The variable shutter is externally adjustable from 0 to 160 deg, and has calibration marking. A simple gear change provides speeds of 20, 40, 60, or 80 frames/sec.

The camera is magazine-adapted to accept a 100-ft daylight loading spool or a 200-ft magazine for darkroom loading. Dimensions are $8 \times 6^{13}/_{16} \times 5^{3}/_{16}$ in. and weight is 7 lb. Optional features and accessories are available.

Deep-Sea Camera for Arctic Ocean Photography

A 35-mm camera, carrying its own light source and enclosed in a metal container built to withstand the tremendous pressures of the ocean depths, has been developed by Dr. Edward M. Thorndike, Research Associate in Geology at the Lamont Observatory, Columbia University.

The equipment has been used to photograph the Arctic Ocean bottom 7000 feet below the surface and about 400 miles from the North Pole. The camera is lowered through a hole in the ice at the end of a wire attached to a winch on the ice floe base. When the camera hits the ocean floor, the impact triggers the light and the film is exposed. The photographs are the first ever made of the ocean bottom in the central polar region. Some of the pictures show puzzling detail such as tracks and large rocks on the ocean floor. As yet scientists have not determined what the tracks are, how they got there,or how long they have been there. It has been assumed that the rocks were floated out on the ocean on ice floats and sank when the ice melted.

The camera is equipped with a Leitz Summaron, 35mm $f/2.5$ lens which is used at approximately $f/8$. It has no shutter as the deep ocean has essentially no light. The camera holds a 20-ft spool of 35mm nonperforated film which is transported by a 6-v 17-ma motor geared to the spool. A GE FT-118 100-wsec electronic flashlamp powered by two 525 mf capacitors charged to 480 v by two 240-v batteries furnishes illumination. Both camera and light are contained in watertight aluminum cases $4^{1}/_{4}$ in. inside diameter.

• Densitometers and Sensitometers

Macbeth-Ansco Electronic Densitometer

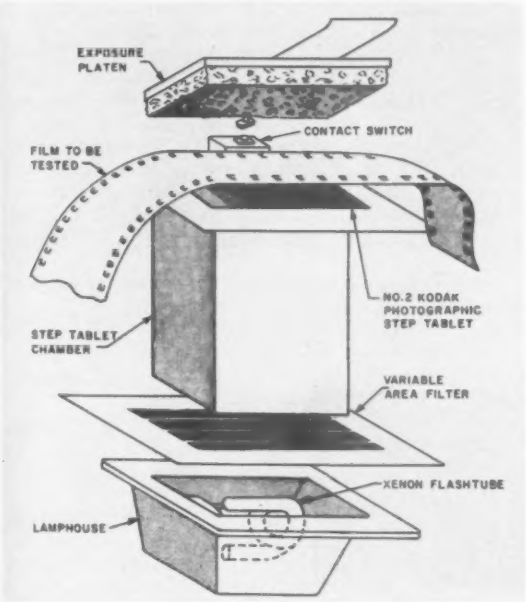
A new electronic densitometer, Macbeth-Ansco Model 12A, capable of furnishing direct density readings from 0 to 4.0 with an accuracy of ± 0.02 density units, has been developed by Macbeth Instrument Corp., Newburgh, N.Y. The densitometer features a dynode-feedback photomultiplier tube circuit which is linear with optical density, and a new fundamental optical system insuring parallel incident light, for measurement of diffuse transmission density independent of light-scattering properties of the sample.

Other features of the densitometer include: separate electronic zeroing for all three colors and for black-and-white and visual density, direct-reading large-

scale meter 0 to 4.0, voltage-stabilized circuit and light source, improved narrow-band-pass color filters, and new color-filter wheel with blanks for easy installation of additional filters. The densitometer is suitable for transmission density measurement of black-and-white and color film, reflection density measurement of black-and-white printing papers and color prints, transmission density measurements of x-ray film and radiation-exposure badges, and many other applications.

Electronic Flash Sensitometer

A new approach to sensitometry is made possible by a development of Edgerton, Germeshausen and Grier, Inc., 160 Brookline Ave., Boston, Mass. The new instrument, called the Mark VI Sensitometer, is an intensity-scale sensitometer employing a xenon-



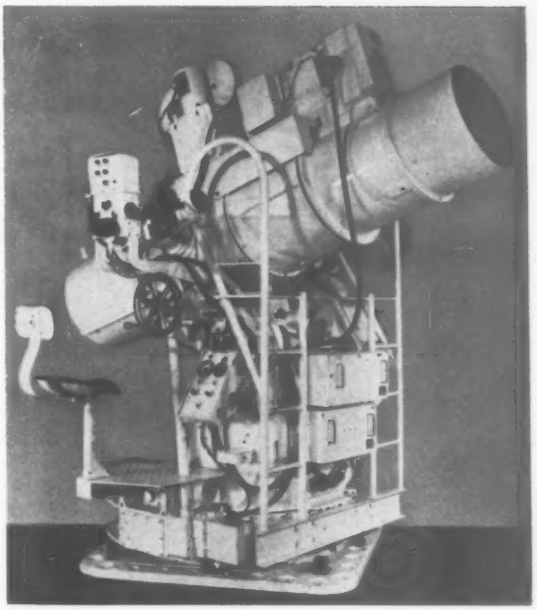
filled flash tube as the light source. Three different capacitor circuits are built into the instrument to provide exposure times of $^1/_{100}$, $^1/_{1000}$, and $^1/_{10,000}$ sec, selected by pushbutton.

The sensitometer is compact in size, convenient to use, repeatable, and automatic. The color of the light does not change materially with use and thousands of flashes can be produced before the amount of light is reduced by a measurable amount.

• Miscellaneous

Igor MK II Tracking Telescope

The Igor MK II Tracking Telescope, designed and manufactured by J. W. Fecker, Inc., Pittsburgh 6, Pa.,



is now undergoing its first field tests at the Air Force Missile Test Center, Patrick Air Force Base, Fla. Six of the telescopes are being supplied for Patrick.

The telescope system is supported on a mount which is moved and controlled smoothly by the manual operation of bandwheels available to two trackers. Visual pickup and retention of the target is made possible by utilizing open sights and visual sighting telescopes. The tracking rate of the instrument is approximately 10 deg/sec in each coordinate.

The main optical system is an 18-in. clear aperture catadioptric telescope with variable focal length from 90 to 500 in. The size of the field, which is approximately 3 in. in diameter, can cover the aperture of a full frame 70mm motion-picture camera. The manufacturer states that under dynamic tracking operation in the field, resolution of 1 sec of arc has been obtained.

Automatic Scanning Correlator (AUSCOR)

The Photographic Survey Corp., Ltd., 1450 O'Connor Dr., Toronto, Ont., has announced a device, known as the Automatic Scanning Correlator (AUSCOR), for the automatic correlation of stereo images. In its present form, AUSCOR is a system of electronics and electromechanics which senses the relative displacement of images in two photographs taken from different positions but having overlapping fields of view. This is equivalent to the perception of depth by the human eye by virtue of their spacing.

According to the company, the device is described by experts as a "major breakthrough in the science of aerial mapping." Although it was developed pri-

marily for use in photogrammetric data reduction, it is expected that numerous other applications of the technique will be found.

"Exicon" for Industrial X-Ray Enhancement

Philco Corp., Government and Industrial Div., 4700 Wissahickon Ave., Philadelphia 44, Pa., has released some details concerning "Exicon" (EXpanded Image CONtrast), an x-ray viewing system that increases the readability of x-ray negatives through contrast enhancement.

The Exicon system consists of a monochrome TV monitor, an operators' console, and a Philco flying-spot scanner. An x-ray negative placed before the flying-spot scanner is magnified and reproduced in enhanced monochrome. Negatives may be quickly shifted about to obtain magnified images of any portion.

Photography Used to Measure Length of Sputnik II

The usefulness of photographic instrumentation in scientific investigation is illustrated by a recent press release from the Perkin-Elmer Corp., Norwalk, Conn. The release gives details of how photography was used to measure the length of Sputnik II, the dog-carrying Soviet satellite.

The length was calculated as 74 to 84 feet from a photo sequence taken on 70mm film using the Recording Optical Tracking Instrument (ROTI) developed and built by the Perkin-Elmer Corp. ROTI has a 24-in. aperture telescope with focal lengths up to 500 in. It was trained on the satellite as it passed over Patrick Air Force Base on Dec. 21, 1957, at about 6:05 p.m.

A series of enlargements shows typical frames from the best or middle part of the photo series at intervals of 2 sec. Approximately 400 ft of film were used.

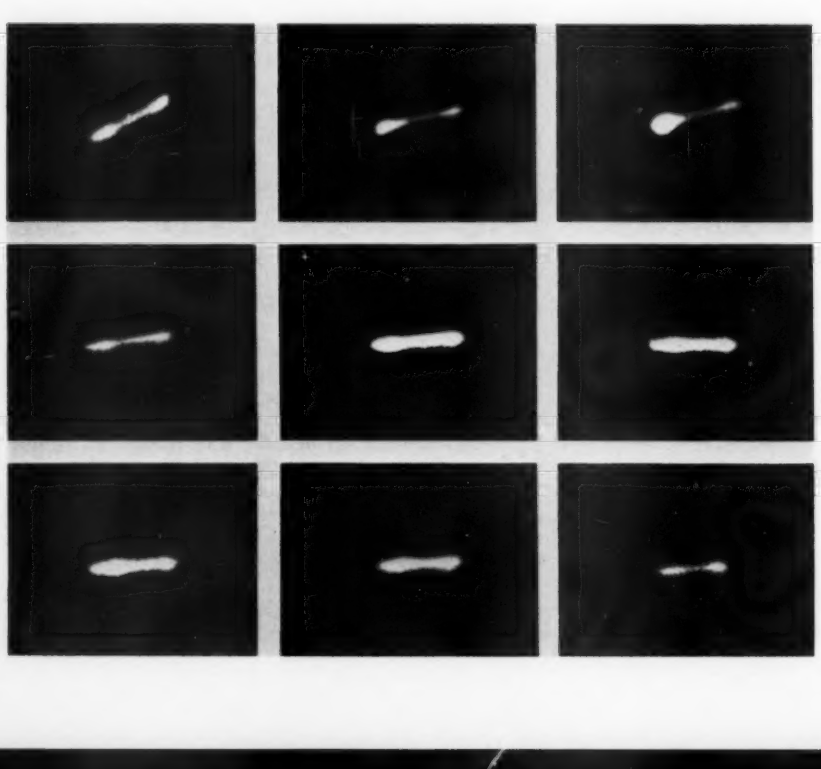
Nine Papers on Instrumentation for Missile Testing

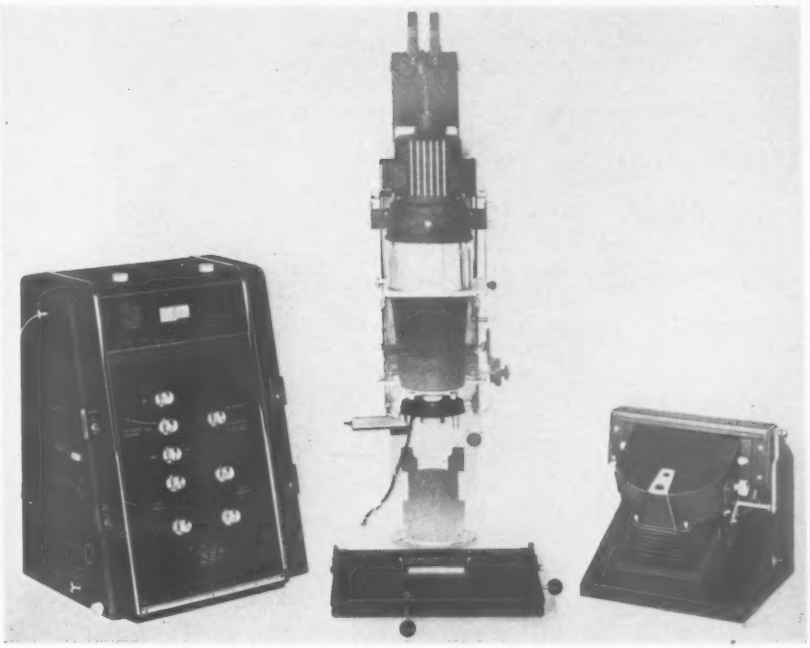
J. SMPTE, 67 (4, Part I): 225–55 (April 1958).

The first of this series of nine papers describes the atmospheric problem, basic theoretical approaches, and prospective results of present programs. Other papers describe specific operations and equipment. Finally there is a group discussion in which diverse specialists seek one another's help. The titles and authors of the papers are as follows:

"Atmospheric Optics," H. C. Schepler; "Visibility Detection and Recording Objects Against a Sky Background," E. P. Martz, Jr.; "Atmospheric Limitations on Missile Photography," Seibert Q. Duntley; "Flying Camera Stations," Floyd A. Kinder; "Optical Tracking Instrumentation," A. H. Schendel; "A Design and Operational Philosophy for an Ultra-Precision Tracking Mount System for a Missile Test Range," John A. Clemente; "Photographic Instrumentation at the Air Proving Ground Center," H. C. Schepler; "Automatic-Exposure Control for a High-Resolution Camera," George Economou, Vladimir Luban, and Morton Mehr; and "Discussion on Missile Photography."

All the papers are illustrated and some have references.





Simmon Omega Tri-Color Computer

Simmon Bros., Inc., 30-28 Starr Ave., Long Island City 1, N.Y., has announced availability of the Omega Tri-Color Computer, which automatically coordinates color and other factors, computes the exposure relationships, and applies the correct exposure through three filters automatically. It automatically compensates for reciprocity failure and eliminates the color drift that otherwise occurs when the magnification ratio is changed.

An advantage of this system is that any deliberate change in color balance does not change the density of the print. Dodging for local color and density correction on a production basis can be performed easily by means of the automatic Omega Dodger. Once the exposures are completed, processing is by standard procedures for normal results.

The Computer is designed primarily for the Omega and Automega D-2, D-3, and E-5 Enlargers, but may be adapted to some other makes.

Pulsed Xenon Arc Lamp

A new light source which features instant starting, effective color, convenient size, and high output has been announced by the General Electric Company, Nela Park, Cleveland, Ohio. Called the Pulsed Xenon Arc Lamp (PXA), it is a tubular, quartz, xenon-gas-filled lamp, designed primarily to expose slow-speed photosensitive materials.

The lamp obtains high efficiency by permitting the current to flow for a very brief interval of time. These short duration, high-current pulses are developed in a special ballast unit which combines a supply transformer, saturable reactor, and capacitor in one unit with no moving parts. With 60 cycle supply, the lamp delivers 120 pulses of light of about $^1/_{1000}$-sec duration. Because the eye integrates these pulses, the lamp appears to burn continuously.

The lamps are made in four sizes according to lighted length; 3-in. 300-w, 12-in. 1000-w, 24-in. 2000-w, and 36-in. 3000-w. The lamp bulbs are Type T-3 with a nominal diameter of $^3/_8$ in. and average life of 50 hr.

A Review of the Methods of High-Speed Photography

S. J. Courtney Pratt, *Reports on Progress in Physics, 20:* 379–432 (1957).

A comprehensive review covering the variety, range, and precision of the methods available for photographic recording of fast phenomena. The capabilities of the newer techniques are considered, and they are classified by the kind of record obtained. Profusely illus., 133 ref.

Photographic Sensitivity

J. W. Mitchell, *Reports on Progress in Physics, 20:* 433–515 (1957).

This paper reviews the experimental and theoretical work on photographic sensitivity and related topics which has been published during the past ten years. New experimental results, obtained to a large extent

with model systems, have necessitated substantial revision and amplification of previously accepted theories. The approach which is followed in this paper leads to an integrated treatment of the whole range of photographic phenomena in which very few hypotheses without direct experimental foundation have to be introduced. Illus., 267 ref.

Applications of Magnetography to Graphic Recording

John B. Gehman, (from a paper presented at the 1958 National Convention, IRE, New York City, Sept. 24–27, 1958).

A high-speed oscillographic recorder is described which uses magnetic tape as the recording medium. The recorder has a frequency response in excess of 10 kc. There are no moving parts in the writing head which induces a latent image in the magnetic tape. The recorder produces a rectilinear trace and simultaneously prints its own timing and calibration lines.

The magnetic tape is driven in excess of 200 in. per sec. and is processed continuously within the same instrument at a rate of 10 in. per sec.

"Elf," a New Electroluminescent Display

E. A. Sack (from a paper presented at the 1958 National Convention, IRE, New York City, Sept. 24–27, 1958).

Modern imaging systems require some sort of flat, bright nonvacuum display with highly flexible storage capabilities. A new approach to such a display is described, in which electroluminescence is utilized as the light source and ferroelectrics are incorporated to provide control and storage of the output image. For convenience, the electroluminescent-ferroelectric screen is called "Elf."

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